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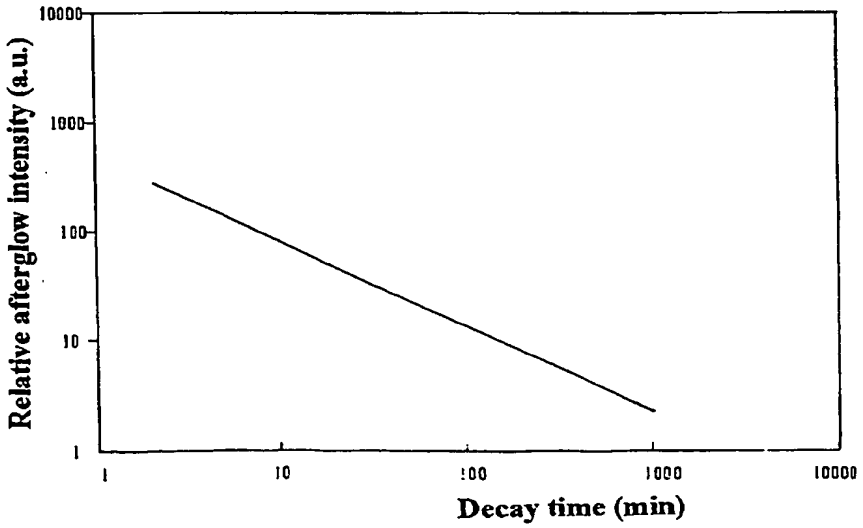
(54) SILICATE PHOSPHOR WITH A LONG AFTERGLOW AND MANUFACTURING METHOD THEREOF

(57) Disclosed is a long afterglow silicate luminescent materials which have a main chemical composition formula of: $aMO \cdot bM'O \cdot cSiO2 \cdot dR: Eu_x,Ln_y$, wherein M represents one or more elements selected from a group consisting of Sr, Ca, Ba and Zn; M' represents one or more elements selected from a group consisting of Mg, Cd and Be; R represents one or two components selected from B_2O_3 and P_2O_5;Ln represents one or more elements selected from a group consisting of Nd, Dy, Ho, Tm, La, Pr, Tb, Ce, Mn, Bi, Sn and Sb; a, b, c, d, x and y are mole coefficients; wherein: $0.6 \le a \le 6$, $0 \le b \le 5$, $1 \le c \le 9$, $0 \le d \le 0.7$, $0.00001 \le x \le 0.2$, and $0 \le y \le 0.3$; these luminescent materials have long afterglow characteristic after absorbing short wavelength lights.

FIG.4



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Description

FIELD OF INVENTION

[0001] This invention relates to phosphor with a long afterglow (i.e. long afterglow luminescent material) and more particularly to long afterglow silicate luminescent material and its manufacturing method.

BACKGROUND OF THE INVENTION

[0002] Since its invention in the nineteenth century, the traditional long afterglow phosphors of ZnS series have been improved greatly, several typical products have been produced, including ZnS:Cu (which emits green light), (CaSr)S:Bi (which emits blue light) and (ZnCd)S:Cu (which emits yellowish-orange light), and they have been applied in some commercial fields, however the shortcoming of these phosphors were: poor stability, easy to decompose in air, easy to turn gray even black when irradiated under sun light, only 0.5-2 hrs short luminescent afterglow time, and luminous brightness was weak etc., all these can not satisfy the requirement for practice use. In order to improve the brightness and afterglow time, radioactive luminescent materials were made, in which some radioactive elements such as Co, Ra, H_3 were added, although such elements can make the phosphor continuously give out light and the phosphor has once been used in air dashboard, clock fields etc.. however, the application of the phosphor was greatly confined due to the radioactive contamination and rather expensive price,.

[0003] The aluminate long afterglow luminescent material was invented at the beginning of the nineties ,as stated in China patent application laid open No.CN1053807A and China patent No.ZL92110744.7,its luminescent brightness ,long afterglow character and stability were obviously superior to the above sulphide series products, and it has already been used in the articles for daily use ,low illumination indicator board, clock etc..

[0004] However these phosphors still have bad anti-moisture character, and they have strict restriction over the raw material's purity and form, besides, the production cost was higher, as well as single luminescent color etc., therefore it also can not satisfy the requirement of usage very well .

[0005] In 1968,T.L. Barry published the research results of luminescent spectrum and excitation spectrum of $Me_3MgSi_2O_8:Eu^{2+}$ (Me=Ca, Sr and Ba) and $Me_2SiO_4:Eu^{2+}$(Me=Sr and Ba)(J. Electrochem.Soc. V115 No. 7, 733-738,1968; V115 No.11, 1181-1184,1968); then T.L. Barry published the research result in luminescent and excitation spectrum of $BaMg_2Si_2O_7:Eu^{2+}$ (J. Electrochem. Soc. V117 No.3, 381-385,1970); Blasse,G etc. published fluorescence of Eu^{2+} activated silicates (Philips Res. Rep.(1968),23(2),189-200) in 1968.However no report on silicate phosphor which having long afterglow property has been published.

SUMMARY OF THE INVENTION

[0006] In order to solve the above problem existed in the prior art, the invention provides a kind of series silicate long afterglow luminescent material that having various luminescent colors ,wide scope spectrum ,better anti-moisture property and nice stability as well as the long afterglow time and high afterglow brightness.

[0007] This invention provides a new type of series long afterglow luminescent material, it is a kind of long afterglow luminescent material which use silicate as main matrix, rare earth ions and other ions as activator , and add some compounds of B or P to make the improvement of long afterglow performance, thus blue, green, yellow etc. multiple colors long afterglow luminescent characters were gained in the silicate system.

[0008] The main chemical composition of long afterglow luminescent material in this invention can be expressed by the formula:

$$aMO \cdot bM'O \cdot cSiO_2 \cdot dR:Eu_x,Ln_y \quad (1)$$

[0009] Wherein

M represents one or more elements selected from a group consisting of Sr(strontium), Ca(calcium), Ba(barium) and Zn(zinc);

M' represents one or more elements selected from a group consisting of Mg(magnesium), Cd(cadmium), and Be(beryllium);

R represents one or two components selected from B_2O_3(boric anhydride) and P_2O_5(di-phosphoruspentoxide);

Ln represents one or more elements selected from a group consisting of Nd(neodymiun), Dy(dysprosium), Ho(holmium), Tm(thulium), La(lanthanum), Pr(praseodymium), Tb(terbium), Ce(cerium), Mn(manganese), Bi(bismuth), Sn(tin), and Sb(antimony);

a, b, c, d, x and y are mole coefficients, wherein :$0.6 \le a \le 6$, $0 \le b \le 5$, $1 \le c \le 9$, $0 \le d \le 0.7$, $0.00001 \le x \le 0.2$, and $0 \le y \le 0.3$;

these luminescent materials can give an emission spectrum between 420-650nm when excited by the short wavelength light of 250-500nm, its peak position is 450-580nm, and the long afterglow luminescent colors are blue, bluish-green, green, greenish-yellow or yellow.

[0010] A preferred group of long afterglow luminescent materials according to this invention can be expressed by the main chemical composition formula (1) , wherein M represents one or two elements selected from Sr and Ca; M' represents Mg;R represents one or two components selected from B_2O_3 and P_2O_5; Ln represents one or more elements selected from a group consisting of Nd, Dy, Ho, Bi and Sn, wherein $0.6 \le a \le 4$, $0.6 \le b \le 4$, $1 \le c \le 5$, and $0 \le d \le 0.4$.

[0011] In a preferred group of long afterglow luminescent materials acccording to this invention , the main matrix compound of the phosphor is : $M_2MgSi_2O_7$ or $M_3MgSi_2O_8$ wherein M represents $Sr_{1-z}Ca_z$, $0 \le z \le 1$.

[0012] In a further preferred group of long afterglow luminescent material according to this invention , the main chemical formula of the phosphor is: $M_2MgSi_2O_7$:Eu,Ln or $M_3MgSi_2O_8$:Eu,Ln, wherein M represents $Sr_{1-z}Ca_z$, $0 \le z \le 1$.

[0013] In the technique of making the long afterglow luminescent material of this invention, the compounds which containing the elements in the formula (1) are used as raw material, the mole proportion of elements in the raw material used to produce the luminescent material are as follows:

M: 0.6-6 R: 0-0.7 in terms of B_2O_3 and P_2O_5
M': 0-5 Eu: 0.00001-0.2
Si: 1-9 Ln:0-0.3

wherein

M represents one or more elements selected from a group consisting of Sr, Ca, Ba and Zn,;
M' represents one or more elements selected from a group consisting of Mg, Cd and Be;
R represents one or two elements selected from B and P;
Ln represents one or more elements selected from a group consisting of Nd, Dy, Ho, Tm, La, Pr, Tb, Ce, Mn, Bi, Sn and Sb;

[0014] Wherein M, M', Ln and Eu can be incorporated in the raw materials in the form of carbonate, sulphate, nitrate, phosphate, borate, acetate, oxalate, citrate, oxide, hydroxide or halogenide of the elements or their mixture; Si can be added in the form of SiO_2,silicic acid , silica gel or silicate; R can be added in the form of any compounds containing B or P, with the proviso that such compounds can form B_2O_3 or P_2O_5 in the subsequent sintering procedure;

[0015] In order to produce the desired phosphor, high temperature solid-phase reaction method is used, first weighted above raw materials according to mole proportion, then ground it into fine and mixed homogeneously by using dry-mixing method, wet-mixing method in with solvents e.g. alcohol, acetone, are added and evaporated after the mixing or chemical reaction sol-gel process method; the mixture is placed in the crucible then sintered at a temperature between 1100~1400 °C in furnace under a reducing atmosphere for about 2 to 50 hours depends on the oven's capacity and mixture's weight, for small amount mixture, it is usually fired for 2-5 hours, the reducing atmosphere is selected from $H_2(g)$, $NH_3(g)$, $N_2(g)+H_2(g)$ and carbon powder, wherein g=gas.

[0016] In order to improve the phosphor's quality, small amount of additives selected from the group consisting of the compounds NH_4Cl, NH_4F, CaF_2, SrF_2, Li_2CO_3, $CaSO_4$, $SrSO_4$,$SrHPO_4$,and $CaHPO_4$ can be added into the raw material. After sintering, the sintered mixture is milled and sifted into desired particle size phosphor.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017]

FIG. 1 represents the emission spectrum(a) and the excitation spectrum(b) of $Sr_2MgSi_2O_7$:Eu phosphor
FIG. 2 represents the x-ray diffraction pattern of $Sr_2MgSi_2O_7$:Eu phosphor
FIG. 3 represents the emission spectrum(a) and the excitation spectrum (b)of $Sr_2MgSi_2O_7$:Eu,Dy phosphor
FIG. 4 represents the afterglow characteristic curve of $Sr_2MgSi_2O_7$:Eu ,Dy phosphor
FIG. 5 represents the emission spectrum(a) and the excitation spectrum(b) of $Ca_2MgSi_2O_7$:Eu,Dy phosphor
FIG. 6 represents the x-ray diffraction pattern of $Ca_2MgSi_2O_7$:Eu,Dy phosphor
FIG. 7 represents the afterglow characteristic curve of $Ca_2MgSi_2O_7$:Eu ,Dy phosphor
FIG. 8 represents the emission spectrum(a) and the excitation spectrum(b) of $(Sr_{0.5}Ca_{0.5})_2MgSi_2O_7$:Eu,Dy phosphor
FIG. 9 represents the x-ray diffraction pattern of $(Sr_{0.5}Ca_{0.5})_2MgSi_2O_7$:Eu,Dy phosphor
FIG. 10 represents the afterglow characteristic curve of $(Sr_{0.5}Ca_{0.5})_2MgSi_2O_7$:Eu,Dy phosphor

FIG. 11 represents the emission spectrum(a) and the excitation spectrum(b) of $(Sr_{0.75}Ca_{0.25})_2MgSi_2O_7$:Eu,Dy phosphor

FIG. 12 represents the emission spectrum(a) and the excitation spectrum(b) of $(Sr_{0.25}Ca_{0.75})_2MgSi_2O_7$:Eu,Dy phosphor

FIG. 13 represents the emission spectrum(a) and the excitation spectrum(b) of $Sr_3MgSi_2O_7$:Eu,Dy phosphor

FIG. 14 represents the x-ray diffraction pattern of $Sr_3MgSi_2O_7$:Eu,Dy phosphor

FIG. 15 represents the emission spectrum(a) and the excitation spectrum(b) of $Ca_3MgSi_2O_8$:Eu,Dy phosphor

FIG. 16 represents the x-ray diffraction pattern of $Ca_3MgSi_2O_8$:Eu,Dy phosphor

FIG. 17 represents the emission spectrum(a) and the excitation spectrum(b) of $Ba_5Si_8O_{21}$:Eu,Dy phosphor

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0018] The measurement of sample's luminescent afterglow in this invention is to put the sample in a 50mm diameter,5mm deep disc, and keep it in dark room for more than 10h,then took it out and put it under standard D65 light 10001x illuminance, after irradiated for 10min use luminance meter measure its brightness changes with time. In the same time, excited the comparative sample under the same conditions, use comparative sample as 100 to count the sample's relative brightness value. For blue afterglow,the comparative sample is (CaSr)S:Bi; for yellow afterglow,the comparative sample is (ZnCd)S:Cu; and for green, bluish-green, greenish-yellow afterglow, the comparative sample is ZnS:Cu. Adopt x-ray diffraction method to define the phosphor's crystal structure and component, measured its x-ray diffraction value, and compared it with card value, so can define its main compound. Adopt fluorescent spectrophotometer to measure the phosphor's emission spectrum and excitation spectrum.

[0019] A lot of research work indicated that in the chemical composition formula, the different of element in M and M', results in the different colors of long afterglow, as well as the different of phosphor's main crystal structure; the change of a, b, and c value have some influences to the brightness, crystal structure and luminescent color; the different elements component in R and Ln and the change of d, x, and y coefficient value have obvious influence to the brightness, whereas have no obvious influence to the main crystal structure.

[0020] TABLE 1 shows a part of experimental results concerning the relationship between luminescent color and M,M',a,b.

[0021] TABLE 1 Experimental condition let c=2.5, d=0.1, $R=B_2O_3$, x=0.005, y=0.04, Ln=Nd, select N_2(90%)+H_2(10%) as reducing atmosphere, synthetic temperature 1250-1320 °C, sintering time 4 hrs.

TABLE 1

Experiment of luminescent color											
Ex	Element	M:	Sr	Ca	Ba	Zn	M':	Mg	Cd	Be	Luminescent color
	coefficient	a:					b:				
1			3	0				1			blue
2			0	3				1			green
3			2	0				1			blue
4			0	2				1			yellow
5			0.5	1.5				1			greenish-yellow
6			1.0	1.0				1			green
7			1.5	0.5				1			bluish-green
8			1	0				2			blue
9			0	1				2			yellow
10			0.2	0.8				1.9	0.1		greenish-yellow
11			0.5	0.5				2			green
12			0.7	0.3				1.9		0.1	bluish-green
13			1	0				3			blue
14			0	1				3			yellow

TABLE 1 (continued)

Experiment of luminescent color											
Ex	Element	M:	Sr	Ca	Ba	Zn	M':	Mg	Cd	Be	Luminescent color
	coefficient	a:					b:				
15			0.25	0.75				3.0			greenish-yellow
16			0.5	0.5				3.0			green
17			0.75	0.25				3			bluish-yellow
18			1	1.8	0.2			1			greenish-yellow
19			1.4	1.4		0.2		1			green
20			2.0	1				1			bluish-green
21			1.4	0.35				1.25			bluish-green
22			1.2	0.3				1.5			bluish-green
23			1.0	0.25				1.75			bluish-green
24			0.875	0.875				1.25			green
25			0.75	0.75				1.5			green
26			0.625	0.625				1.75			green
27			0.525	1.225				1.25			greenish-yellow
28			0.45	1.05				1.5			greenish-yellow
29			0.375	0.875				1.75			greenish-yellow
30			0.363	1.487				1.25			light yellow
31			0.225	1.275				1.5			light yellow
32			0.187	1.063				1.75			light yellow

[0022] When M represents Sr or represents Sr,Ca,Ba and Zn, wherein Sr is the main element, Ca, Ba, and Zn are secondary elements, M' represents Mg or represents Mg,Cd and Be, wherein Mg is the main element, Cd and Be are secondary elements, the synthetic phosphor can presents blue—bluish-green afterglow luminescence after irradiated by short wavelength light of 250-450nm. Experiments indicate that the different value of a, b and c has certain influence to the phosphor's luminescent brightness and structure, when $0.6 \le a \le 4$, $0.6 \le b \le 4$ and $1 \le c \le 5$, the phosphor presents brighter blue—bluish-green luminescent color, when $1.5 \le a \le 2$, $0.6 \le b \le 2$, and $1.5 \le c \le 2.5$, according to the x-ray diffraction pattern, the main matrix compound of the phosphor is defined as $Sr_2MgSi_2O_7$ as well as its crystal structure, see FIG. 2; when exceed the above coefficient scope, there may appear $Sr_2MgSi_2O_7$ compound, but the more other compounds exist too; when $2.7 \le a \le 3.3$, $0.8 \le b \le 1.2$ and $1.7 \le c \le 2.3$, the phosphor's main compound is $Sr_3MgSi_2O_8$, see FIG.14.

[0023] When M represents Ca or represents Ca,Sr,Ba and Zn, wherein Ca is the main element, Sr, Ba and Zn are secondary elements, M' represents Mg or represents Mg,Cd and Be, wherein Mg is the main element, Cd and Be are secondary elements, the synthetic phosphor can presents green-yellow afterglow luminescent color after irradiated by the short wavelength light of 250-500nm. The same experiment indicates that the different value of a, b and c has certain influence to the phosphor's luminescent brightness and structure, when $0.6 \le a \le 4$, $0.6 \le b \le 4$, $1 \le c \le 5$, the phosphor presents brighter green—yellow luminescence, when $1.5 \le a \le 2.4$, $0.6 \le b \le 2$, and $1.5 \le c \le 2.5$, according to the x-ray diffraction pattern, the main matrix compound of the phosphor is defined as $Ca_2MgSi_2O_7$ as well as its crystal structure, see FIG. 6; when exceed the above coefficient scope, there may appear $Ca_2MgSi_2O_7$ compound, but the other compounds are more than the former; when $2.7 \le a \le 3.3$, $0.8 \le b \le 1.2$, and $1.7 \le c \le 2.3$, the phosphor's main matrix compound is $Ca_2MgSi_2O_8$, see FIG. 16.

[0024] When M represents Sr and/or Ca, for easy to show ,adopt formula $Sr_{1-z}Ca_z$, wherein $0 \le z \le 1$, or represent $Sr_{1-z}Ca_z$, Ba and Zn, wherein $Sr_{1-z}Ca_z$ are the main element, Ba and Zn are secondary elements, M' represents Mg or represents Mg, Cd and Be, wherein Mg is the main element, Cd and Be are secondary elements, with the change of z value, the synthetic phosphor presents blue— bluish-green—greenish-yellow—yellow afterglow luminescence: when z=0, color is blue; z=1, it's green—yellow; $0<z<0.5$, mainly is bluish-green—green color; $0.5<z<1$, mainly is green—greenish-yellow color; z=0.5 or near it is green. Just the same, the different values of a, b and c have certain influence

to the phosphor's luminescent brightness and structure, when $0.6 \leq a \leq 4$, $0.6 \leq b \leq 4$ and $1 \leq c \leq 5$, the phosphor presents bluish-green, green and greenish-yellow afterglow luminescent color, when $1.5 \leq a \leq 2.4$ $0.6 \leq b \leq 2$ and $1.5 \leq c \leq 2.5$, analyzed its diffraction pattern, it is similar to that of $Sr_2MgSi_2O_7$ and $Ca_2MgSi_2O_7$, considering with the element's match, the phosphor's main matrix compound can be deduced as $(Sr_{1-z}Ca_z)_2MgSi_2O_7$, see FIG. 9; when the above coefficients scope are exceeded, the compound of $(Sr_{1-z}Ca_z)_2MgSi_2O_7$ can also be appeared, but there are more other components.

[0025] Refer to the luminescent material's formula in Luminescence, when the crystal structure of phosphor have not yet been defined, it can be expressed by the main component of the phosphor, that is expressed by chemical composition formula; when the main compound and the crystal structure of the phosphor is defined, it should be expressed by chemical formula in this invention.

[0026] According to the compound and crystal structure of the above phosphor in this invention, the main chemical formula of this phosphor is: $M_2MgSi_2O_7$:Eu, Ln or $M_3MgSi_2O_8$:Eu, Ln, wherein M presents $Sr_{1-z}Ca_2$, $0 \leq z \leq 1$.

[0027] When M represents Ba ,$4 \leq a \leq 6$, b=0 and $6 \leq c \leq 9$, the phosphor presents light green afterglow, according to x-ray diffraction pattern, its main compound is defined as $Ba_5Si_8O_{21}$,so the main chemical formula of this phosphor is $Ba_5Si_8O_{21}$:Eu,Ln.

[0028] When M represents Zn, $1 \leq a \leq 3$, b=0 and $0.7 \leq c \leq 1.5$, the phosphor presents light green afterglow, according to x-ray diffraction pattern, its main compound is defined as Zn_2SiO_4,so the main chemical formula of this phosphor is Zn_2SiO_4,:Eu,Ln.

[0029] When M represents $Sr_{1-z}Ca_z$ $0 \leq z \leq 1$, M' represents Mg, where 0-40% mol M and/or M' can be replaced by one or more elements selected from a group consisting of Ba, Zn, Cd and Be, the phosphor has long afterglow property, especially when 5-20% mol M and/or M' replaced by one or two of Ba and Cd, the phosphor have good luminescent performance.

[0030] In chemical composition formula, without R and/or Ln element (that is when d and/or y is zero),the synthetic phosphor can also give out afterglow. If R and/or Ln exist in the phosphor, its luminescent afterglow intensity has been strengthened obviously, certainly the mole coefficient d and y may affect the afterglow luminescent intensity, adding different elements of Ln causes different luminescent intensity, two or more elements' adding will be even better than that of single element in luminescent effect.

[0031] When y=0, the phosphor's chemical composition formula is $aMO \cdot bM'O \cdot cSiO_2 \cdot dR:Eu_x$, Eu is the activator, its emission spectrum is characterized by Eu^{2+}, that means Eu is the main activator ,the afterglow luminescent intensity changes with x value,, the suitable scope of x is :$0.00001 \leq x \leq 0.2$.

[0032] When y>0, Ln exists in the phosphor, the experiment indicate that when one or more elements of Nd, Dy, Ho, Tm, La, Pr, Tb, Ce, Mn, Bi, Sn and Sb are doped, it will have certain enhance in phosphor's luminescent intensity, especially obvious effect can be seen in Nd,Dy,Ho,Bi and Sn , experiment indicate that when $0 < y \leq 0.3$, it has obvious enhancement function to the phosphor, whose afterglow luminescent intensity are much higher and the decay time are much longer than that of without Ln, see experiment in TABLE 2-10, according to the Luminescence theory, it can act as co- activator function.

[0033] When d=0, the phosphor's chemical composition formula is $aMO \cdot bM'O \cdot cSiO_2 \cdot dR:Eu_x,Ln_y$, this phosphor presents certain long afterglow effect the afterglow luminescent intensity changes with x and y value.

[0034] When d>0,the adding of R component can obviously improve the phosphor's long afterglow luminescent intensity compared with that of d=0, the R component of the phosphor can be the compounds of B or p, i.e. B_2O_3, H_3BO_3, P_2O_5, H_3PO_4, $(NH_4)_2HPO_4$, $NH_4H_2PO_4$ etc., adding of these components can improve the phosphor's long afterglow luminescent intensity, reduce the phosphor's synthetic temperature, improve the phosphor's synthetic quality, and loosened the powder of synthetic phosphor, increase the product rate.

[0035] The influence of R component to the phosphor's luminescent property, see TABLE 2.

[0036] TABLE 2 Select bluish-green phosphor in this experiment, let $M=Sr_{0.75}Ca_{0.25}$, M'=Mg, $R=B_2O_3$ and/or P_2O_5, Ln=Dy, a=1.5, b=1.5, c=2.5, x=0.01, y=0.08, NH_3(g) as reducing atmosphere, and synthetic temperature at 1280 °C.

TABLE 2

The R and Ln component function experiment			
Ex	Chemical composition formula	Relative intensity	afterglow
		10°	60°
1	$1.5(Sr_{0.75}Ca_{0.25})O \cdot 1.5MgO \cdot 2.5SiO_2:Eu_{0.01}$	40.1	102
2	$1.5(Sr_{0.75}Ca_{0.25})O \cdot 1.5MgO \cdot 2.5SiO_2:0.1B_2O_3:EU_{0.01}$	114	176
3	$1.5(Sr_{0.75}Ca_{0.25})O \cdot 1.5MgO \cdot 2.5SiO_2:0.5P_2O_3:Eu_{0.01}$	94.6	137

TABLE 2 (continued)

The R and Ln component function experiment			
Ex	Chemical composition formula	Relative intensity	afterglow
		10°	60°
4	$1.5(Sr_{0.75}Ca_{0.25})O \cdot 1.5MgO \cdot 2.5SiO_2:0.1B_2O_3 \cdot 0.05P_2O_5:Eu_{0.01}$	121	182
5	$1.5(Sr_{0.75}Ca_{0.25})O \cdot 1.5MgO \cdot 2.5SiO_2:Eu_{0.01}Dy_{0.08}$	772	1540
6	$1.5(Sr_{0.75}Ca_{0.25})O \cdot 1.5MgO \cdot 2.5SiO_2:0.1B_2O_3:Eu_{0.03}Dy_{0.08}$	2541	4808
7	$1.5(Sr_{0.75}Ca_{0.25})O \cdot 1.5MgO \cdot 2.5SiO_2:0.05P_2O_3:Eu_{0.03}Dy_{0.08}$	1724	3946
8	$1.5(Sr_{0.75}Ca_{0.25})O \cdot 1.5MgO \cdot 2.5SiO_2:0.1B_2O_3 \cdot 0.05P_2O_5:Eu_{0.01}Dy_{0.08}$	2638	4972

[0037] The influence of R's amount to the phosphor's luminescent property ,show in TABLE 3. TABLE 3 select blue and green phosphor, in experiment 1-8, let M=Sr, M'=Mg, a=2, b=1, c=2, $R=B_2O_3$, x=0.004.

[0038] Experiment 9-14 is green phosphor, wherein $M=Sr_{0.5}Ca_{0.5}$, M'=Mg, a=2, b=1, c=2.3, $R=P_2O_5$, Ln=Dy ,x=0.004, y=0.01.

TABLE 3

The effect of R component experiment:						
Ex.	Chemical composition formula	R (raw material)	d	Relative afterglow intensity		synthesizing temperature (C°)
				10'	60'	
1	$2SrO \cdot MgO \cdot 2SiO_2:Eu_{0.004}$	0	0	37.4	100	1350
2	$2SrO \cdot MgO \cdot 2SiO_2 \cdot 0.01B_2O_3:Eu_{0.004}$	$2H_3BO_3$	0.01	78.7	115.4	1340
3	$2SrO \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.004}$	$2H_3BO_3$	0.05	134.8	169.2	1330
4	$2SrO \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3:Eu_{0.004}$	$2H_3BO_3$	0.1	132.4	158.5	1320
5	$2SrO \cdot MgO \cdot 2SiO_2 \cdot 0.2B_2O_3:Eu_{0.004}$	$2H_3BO_3$	0.2	109.2	127	1310
6	$2SrO \cdot MgO \cdot 2SiO_2 \cdot 0.3B_2O_3:Eu_{0.004}$	$2H_3BO_3$	0.3	94.5	102	1280
7	$2SrO \cdot MgO \cdot 2SiO_2 \cdot 0.5B_2O_3:Eu_{0.004}$	$2H_3BO_3$	0.5	73.4	96.4	1230
8	$2SrO \cdot MgO \cdot 2SiO_2 \cdot 0.7B_2O_3:Eu_{0.004}$	$2H_3BO_3$	0.7	42.1	74.2	1150
9	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2.3SiO_2:Eu_{0.004}Dy_{0.01}$	0	0	482.4	1263.2	1350
10	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2.3SiO_2 \cdot 0.05P_2O_5:Eu_{0.004}Dy_{0.01}$	$2NH_4H_2PO_4$	0.05	613	1804	1340
11	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2.3SiO_2 \cdot 0.1P_2O_5:Eu_{0.004}Dy_{0.01}$	$2NH_4H_2PO_4$	0.1	1034	2542	1320
12	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2.3SiO_2 \cdot 0.2P_2O_5:Eu_{0.004}Dy_{0.01}$	$2NH_4H_2PO_4$	0.2	807	2326	1310
13	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2.3SiO_2 \cdot 0.3P_2O_5:Eu_{0.004}Dy_{0.01}$	$2NH_4H_2PO_4$	0.3	721	1702	1250

TABLE 3 (continued)

The effect of R component experiment:						
Ex.	Chemical composition formula	R (raw material)	d	Relative afterglow intensity		synthesizing temperature (C°)
				10'	60'	
14	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2.3SiO_2 \cdot 0.5P_2O_5:Eu_{0.004}Dy_{0.01}$	$2NH_4H_2PO_4$	0.5	501	1271	1200

[0039] Experiment indicates when $0<d\leq0.7$, the phosphor's luminescent intensity can be influenced, the amount of R(d) at $0<d\leq0.4$ is better. The exist of R component, analyzed from phosphor's x-ray diffraction pattern, have no obvious influence on the above phosphor's crystal structure and compound, its main compound is silicate component, however, B and P elements existed in phosphor are defined by spectrometric analysis , that means the phosphor contains B and P components, according its chemical composition, marked as B_2O_3 and P_2O_5.

[0040] A part of the long afterglow luminescent materials in this invention is described as follows:

(1)Blue long afterglow luminescent material

[0041] When M=Sr, M'=Mg, R=B_2O_3,a=2, b=1, c=2, d=0.1, the phosphor's chemical composition formula is :$2SrO\text{-}MgO\text{-}2SiO_2\text{-}0.1B_2O_3:Eu_x,Ln_y$, change the value of x, the elements of Ln and the value of y, the experiment results shown in TABLE 4.

TABLE 4

Experiment	Chemical composition formula	Relative afterglow intensity 10'	60'
1-1	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.0001}$	67	114
1-2	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.0004}$	81	122
1-3	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.001}$	124	143
1-4	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}$	136	178
1-5	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.001}$	130	167
1-6	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.01}$	91	121
1-7	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.2}$	80	102
2-1	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Nd_{0.001}$	621	734
2-2	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Nd_{0.003}$	884	896
2-3	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Nd_{0.01}$	1130	1175
2-4	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Nd_{0.04}$	1527	1847
2-5	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Nd_{0.1}$	862	859
2-6	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Nd_{0.5}$	645	692
3-1	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Dy_{0.0005}$	592	913
3-2	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Dy_{0.004}$	927	1754
3-3	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Dy_{0.01}$	1108	2100
3-4	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Dy_{0.04}$	1658	3947
3-5	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Dy_{0.08}$	1421	3136
3-6	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Dy_{0.15}$	1215	2306
3-7	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Dy_{0.3}$	823	1214
4-1	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Ho_{0.0004}$	827	1512
4-2	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Ho_{0.001}$	1014	1894
4-3	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Ho_{0.05}$	1472	2246
4-4	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Ho_{0.1}$	1034	1675
5-1	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Tm_{0.001}$	289	310
5-2	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Tm_{0.05}$	378	420
5-3	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Tm_{0.1}$	384	456
6-1	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}La_{0.001}$	204	189
6-2	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}La_{0.005}$	235	267
6-3	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}La_{0.02}$	269	317
7-1	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Pr_{0.001}$	275	292
7-2	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Pr_{0.004}$	254	264
7-3	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Pr_{0.02}$	250	253
8-1	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Tb_{0.001}$	224	267
8-2	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Tb_{0.004}$	284	368
8-3	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Tb_{0.02}$	230	276

9-1	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Ca_{0.0017}$	278	367
9-2	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Ca_{0.007}$	238	262
9-3	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Ca_{0.0027}$	224	237
10-1	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Mn_{0.001}$	264	290
10-2	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Mn_{0.005}$	273	287
10-3	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Mn_{0.02}$	232	264
11-1	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Bi_{0.001}$	254	347
11-2	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Bi_{0.005}$	314	472
11-3	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Bi_{0.02}$	421	564
12-1	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Sb_{0.0016}$	195	227
12-2	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Sb_{0.006}$	184	215
12-3	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Mn_{0.025}$	147	169
13-1	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Sn_{0.001}$	124	138
13-2	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Sn_{0.005}$	278	367
13-3	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Sn_{0.02}$	167	236
14-1	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Nd_{0.02}Dy_{0.01}$	1831	3150
15-1	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Nd_{0.02}Sn_{0.01}$	1672	2804
16-1	$2SrO{\cdot}MgO{\cdot}2SiO_2{\cdot}0.1B_2O_3{\cdot}Eu_{0.004}Dy_{0.02}Bi_{0.01}$	1837	4356
Comparative sample	Zn:S:Cu	100	100

[0042] The experimental phosphor shown in TABLE 4 can display blue afterglow luminescence after irradiated under sun light, fluorescent lamp or ultraviolet lamp; when excited under 365nm ultraviolet light, it can give 420-550nm broad band emission spectrum, with peak position near 469nm; its excitation spectrum is 250-450nm broad band spectrum, when monitoring at 469nm, indicate this phosphor has strong absorbing ability to short wavelength light, its main matrix compound is defined as $Sr_2MgSi_2O_7$ through x-ray diffraction pattern, the peak position of spectrum can exert certain shift for the different adding component. FIG.1 (a),(b) and FIG.2 are emission spectrum, excitation spectrum and x-ray diffraction pattern of the experimental phosphor 1-4 respectively, whose emission spectrum peak position is 469nm; FIG.3(a),(b) are emission spectrum and excitation spectrum of the experimental phosphor 3-4,its emission spectrum peak position is 470nm.

1.If y=0 in the chemical composition formula, that means no Ln ion exist, the amount of Eu(x) added may have certain influence to afterglow intensity, shown as experiment 1-1~7 in TABLE 4. Compared with comparative sample (CaSr)S:Bi, this phosphor presents certain long afterglow luminescent effect. Further experiment indicates that when the Eu's amount x is less than 0.00001 mol or more than 0.2 mol, its luminescent intensity is weak, so $0.00001 \le x \le 0.2$ is defined.

2.If x=0.004, Ln=Nd, the afterglow intensity corresponding to the changes of the amount of Nd(y) added, see experiment 2-1~6 in TABLE 4, $0.0001 \le y \le 0.3$ are suitable for the amount of Nd(y) added, it can be seen that afterglow intensity is obviously stronger than that of experiment 1-1~7, this indicate that the adding of Nd can strengthen the phosphor's luminescent performance. Draw a log-log afterglow afterglow characteristic curve concerning the phosphor's luminescent afterglow varies with the decay time, this curve is almost a straight line, its decay time can prolong to more than 20 hrs when afterglow brightness reach the eye's lowest visual luminosity 0.32mcd/m^2.

3.If x=0.004, Ln=Dy, the afterglow effect corresponding the change of the amount of Dy(y) added ,see experiment 3-1~7 in TABLE 1,$0.0001 \le y \le 0.3$ are suitable for the amount of Dy(y) added, it can be seen that afterglow intensity is obviously stronger than that of experiment 1-1~7, this indicates that the adding of Dy strengthened the phosphor's luminescent performance. Draw a log-log afterglow characteristic curve concerning the phosphor's luminescent afterglow varies with the decay time, this curve was almost a straight line, see FIG.4, its decay time can

prolong to more than 35 hrs by eye's lowest visual luminosity.

4.If x=0.004, Ln is Ho, Tm, La, Pr, Tb, Ce, Mn, Bi, Sb, Sn and double elements Nd, Dy; Nd, Sn; and Dy, Bi respectively ,its afterglow effect that corresponding the amount of Ly(y) added ,see experiment 4~16 in TABLE 4.

[0043] From the above results, it can be seen that these phosphor's luminescent afterglow effect are obviously superior to that of the comparative phosphor. Especially the adding of Nd, Dy, Ho, Bi, Sn makes the effect even better. According to the crystal structure and main compound of the above phosphor, the blue series phosphor's chemical formula is $Sr_2MgSi_2O_7$:Eu,Ln.

(2)Yellow long afterglow luminescent material

[0044] When M=Ca, M'=Mg, R=B_2O_3, a=2, b=1, c=2, d=0.15, the phosphor's chemical composition formula is: $2CaO \cdot MgO \cdot 2SiO_2 \cdot 0.15B_2O_3:Eu_x,Ln_y$, change the value of x, the elements of Ln, and the value of y, its experimental results shown in TABLE 5.

TABLE 5

Experiment	Chemical composition formula	Relative afterglow intensity	
		10'	60'
1-1	$2CaO \cdot MgO \cdot 2SiO_3 \cdot 0.IB_2O_3 \cdot Eu_{0.0001}$	127	217
1-2	$2CaO \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3 \cdot Eu_{0.0004}$	201	404
1-3	$2CaO \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3 \cdot Eu_{0.001}$	238	417
1-4	$2CaO \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3 \cdot Eu_{0.004}$	223	389
1-5	$2CaO \cdot MgO \cdot 2SiO_2 -0.1B_2O_3 \cdot Eu_{0.001}$	152	345
1-6	$2CaO \cdot MgO \cdot 2SiO_2 -0.1B_2O_3 \cdot Eu_{0.001}$	56	127
1-7	$2CaO \cdot MgO \cdot 2SiO_2 -0.1B_2O_3 \cdot Eu_{0.2}$	45	87
2-1	$2CaO \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3 \cdot Eu_{0.004}Dy_{0.0005}$	387	1071
2-2	$2CaO \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3 \cdot Eu_{0.0004}\ Dy_{0.01}$	832	1324
2-3	$2CaO \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3 \cdot Eu_{0.001}\ Dy_{0.005}$	914	1451
2-4	$2CaO \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3 \cdot Eu_{0.004}\ Dy_{0.15}$	597	921
3-1	$2CaO \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3 \cdot Eu_{0.004}Nd_{0.0002}$	512	714
3-2	$2CaO \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3 \cdot Eu_{0.004}Nd_{0.01}$	490	837
4-1	$2CaO \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3 \cdot Eu_{0.004}Ho_{0.01}$	482	694
4-2	$2CaO \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3 \cdot Eu_{0.004}Ho_{0.05}$	531	728
5-1	$2CaO \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3 \cdot Eu_{0.004}Tm_{0.01}$	417	623
5-2	$2CaO \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3 \cdot Eu_{0.004}Tm_{0.05}$	465	704
6-1	$2CaO \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3 \cdot Eu_{0.004}Ce_{0.0015}$	317	572
6-2	$2CaO \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3 \cdot Eu_{0.004}Ce_{0.005}$	354	643
7-1	$2CaO \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3 \cdot Eu_{0.004}Sn_{0.001}$	397	845
7-2	$2CaO \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3 \cdot Eu_{0.004}Sn_{0.004}$	492	897
8-1	$2CaO \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3 \cdot Eu_{0.004}Bi_{0.001}$	426	823
8-2	$2CaO \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3 \cdot Eu_{0.004}Bi_{0.04}$	549	864
9-1	$2CaO \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3 \cdot Eu_{0.004}Dy_{0.02}Nd_{0.01}$	965	1534
10-1	$2CaO \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3 \cdot Eu_{0.004}Dy_{0.02}Bi_{0.01}$	873	1424
Comparative sample	(ZnCd)S:Cu	100	100

[0045] The experimental phosphor can display yellow afterglow luminescence after irradiated under sunlight, fluorescent lamp or ultraviolet lamp; when excited under 365nm ultraviolet light the phosphor can give 420-650nm wide band emission spectrum, peak value at 535nm; its excitation spectrum is broad band spectrum between 250-500nm when monitoring at 535nm, indicates this phosphor has strong absorbing ability to short wavelength light; its main matrix compound is defined as $Ca_2MgSi_2O_7$; Due to the different adding components, its spectrum peak position can be shifted certain displacement. FIG.5(a),(b) and FIG.6 are the emission spectrum, excitation spectrum and x-ray diffraction pattern of the experimental phosphor 2-3 respectively, its emission spectrum peak position is at 535nm.

1.If y=0 in the chemical composition formula, the amount of Eu(x) added can has certain influence to the afterglow intensity, see the experiment 1-1~7 in TABLE 5.

2.If x=0.004, Ln=Dy, the relationship between the amount of Dy(y) added and the afterglow effect shown in TABLE 5 of experiment 2-1~4 ,it can be seen that the adding of Dy enhance the phosphor's luminescent performance, experiment indicate that $0.0001 \le y \le 0.2$ are better for the amount of Dy added, FIG.7 is log-log characteristic curve of experiment 2-3 phosphor's luminescent afterglow changes with the decay time.

3.If x=0.004, Ln is Nd, Ho, Tm, Ce, Sn, Bi and double Dy, Nd and Dy, Bi respectively, the relationship between the adding amount and afterglow effect are superior to that of comparative sample. According to the above phosphor's main compound, the chemical formula of the yellow series phosphor is $Ca_2MgSi_2O_7$:Eu,Ln.

(3)Green long afterglow luminescent material

[0046] When $M=Sr_{0.5}Ca_{0.5}$, M'=Mg, $R=B_2O_3$, a=2, b=1, c=2, d=0.05, the chemical composition formula is: $2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 0.05B_2O_3 : Eu_x,Ln_y$, change the value of x, the elements of Ln, and the value of y, its experimental results shown in TABLE 6.

TABLE 6

Experiment	Chemical composition formula	Relative afterglow intensity	
		10'	60'
1-1	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.005}$	89.5	226.3
1-2	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.001}$	105.3	247.4
1-3	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.004}$	89.5	323
1-4	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.01}$	52.6	215
1-5	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.02}$	42.1	110.5
1-6	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.1}$	21	57.9
2-1	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.005}Dy_{0.0005}$	562	1515
2-2	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.005}Dy_{0.004}$	1237	3333
2-3	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.005}Dy_{0.008}$	1206	3158
2-4	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.005}Dy_{0.04}$	1246	3421
2-5	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.005}Dy_{0.08}$	1219	3591
3-1	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.005}Nd_{0.0064}$	1127	2815
3-2	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.005}Nd_{0.008}$	1212	3032
3-3	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.005}Nd_{0.16}$	1146	3012
4-1	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.005}Ho_{0.01}$	472	1324
4-2	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.005}Ho_{0.05}$	534	1427
5-1	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.005}Tm_{0.01}$	567	1624
5-2	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.005}Tm_{0.05}$	621	1735
6-1	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.005}Ce_{0.0015}$	116	184
6-2	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.005}Ce_{0.005}$	95	174

TABLE 6 (continued)

Experiment	Chemical composition formula	Relative afterglow intensity	
		10'	60'
6-3	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.005}Ce_{0.02}$	116	216
7-1	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.005}Sn_{0.001}$	118	267
7-2	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.005}Sn_{0.005}$	234	349
7-3	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.005}Sn_{0.02}$	121	254
8-1	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.005}Tb_{0.0013}$	89.5	231.6
8-2	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.005}Tb_{0.0053}$	94.7	242
8-3	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.005}Tb_{0.021}$	31.6	368
9-1	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.005}Pr_{0.0015}$	52.6	136.8
9-2	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.005}Pr_{0.006}$	73.7	194.7
9-3	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.005}Pr_{0.023}$	89.5	226.3
10-1	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.005}Bi_{0.001}$	154	317
10-2	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.005}Bi_{0.005}$	282	431
10-3	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.005}Bi_{0.002}$	297	442
11-1	$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3:Eu_{0.005}Dy_{0.02}Bi_{0.01}$	2042	4127
Comparative sample	ZnS:Cu	100	100

[0047] The experimental phosphor in TABLE 6 can display green afterglow luminescence after irradiated under sunlight, fluorescent lamp or ultraviolet lamp; when excited under 365nm ultraviolet light, the phosphor can give 430-600nm broad band emission spectrum, peak position near 500nm;its excitation spectrum is broad band spectrum between 250-460nm, when monitoring at 500nm, indicated that this phosphor has stronger absorption ability for the short wave light; analyzed from x-ray diffraction patterns, it can be seen that this phosphor diffraction patterns is similar to that of $Sr_2MgSi_2O_7$ and $Ca_2MgSi_2O_7$, concerning the mole proportion of Sr and Ca, the main matrix compound $(Sr_{0.5}Ca_{0.5})_2MgSi_2O_7$ can be deduced. For different addings, its peak position of spectrum can be shifted certain. FIG. 8(a),(b) and FIG.9 are emission spectrum, excitation spectrum and x-ray diffraction pattern of experimental phosphor 2-5 respectively, its emission spectrum peak position is 500nm.

1.If y=0 in the chemical composition formula, the relationship between the amount of Eu(x) added and afterglow intensity ,see experiment 1-1~6 in TABLE 6.

2.If x=0.005, Ln=Dy,the relationship between the amount of Dy(y) and afterglow effect, see experiment 2-1~6 in TABLE 6. It can be seen that this phosphor has obviously strengthened in afterglow intensity compared with the phosphor of experiment 1-1~6. FIG.10 is the log-log characteristic curve concerning luminescent afterglow of phosphor in experiment 2-5 varies with the decay time, it indicates that the decay time can prolong to more than 50hrs when afterglow brightness reach the eye's lowest visual luminosity 0.32mcd/m^2.

3.If x=0.005,Ln=Nd, the relationship between the amount of Nd(y) added and the afterglow effect, see experiment 3-1~3 in TABLE 6, it can be seen that afterglow intensity is higher and decay time is longer.

4.If x=0.005, Ln is Ho, Tm, Ce, Sn, Tb, Pr and Bi respectively, the influence of its adding amount to the afterglow intensity, see experiment 4-10 in TABLE 6.

5.If x=0.005, Ln=Dy and Bi, if Dy and Bi are both added in the same time, then obvious enhancement of luminescent afterglow intensity can be seen, see experiment 11 in TABLE 6.

[0048] According to the main compound of above phosphor, the chemical formula of the green series phosphor is: $(Sr_{0.5}C_{0.5})_2MgSi_2O_7$:Eu,Ln.

(4) Bluish-green to greenish-yellow long afterglow luminescent materials

[0049] When $M=Sr_{1-z}Ca_z$, M'=Mg, $R=B_2O_3$, a=2, b=1, c=2, d=0.1, the phosphor's chemical composition formula is:

[0050] $2(Sr_{1-z}Ca_z)O \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3:Eu_x,Ln_y 0 \leq z \leq 1$, the phosphors' afterglow colors change from blue to

yellow with the z value , when z=0,the color is blue; z=1, which is yellow; z=0.5,which is green. The phosphors' luminescent colors present the change from blue to green then yellow with the change of z value from 0 to 1, that means to change the proportion of Sr and Ca.

1.As shown in TABLE 7, test the influence of the change of the proportion Sr and Ca in $2(Sr_{1-z}Ca_z)O \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3:Eu_{0.004},Dy_{0.02}$, to the emission spectrum peak position, it can be seen that the emission spectrum peak position changed from 469nm to 535nm varies as the z value changes from 0 to 1,this cause the luminescent color presents the change of blue, bluish-green, green, greenish-yellow and yellow, see TABLE 7.

TABLE 7

Z	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1
Sr	Sr	$Sr_{0.9}$	$Sr_{0.8}$	$Sr_{0.7}$	$Sr_{0.6}$	$Sr_{0.5}$	$Sr_{0.4}$	$Sr_{0.3}$	$Sr_{0.2}$	$Sr_{0.1}$	0
Ca	0	$Ca_{0.1}$	$C_{0.2}$	$C_{0.3}$	$C_{0.4}$	$Ca_{0.5}$	$Ca_{0.6}$	$Ca_{0.7}$	$Ca_{0.8}$	$Ca_{0.9}$	Ca
Emission spectra peak, nm	469	473	482	485	496	500	505	509	517	532	535

2.When z=0.25, select chemical composition formula $2(Sr_{0.75}Ca_{0.25})O \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O3_3:Eu_{0.004},Ln_{0.02}$to do experiment, shown as experiment 1~6 in TABLE 8, the phosphors present bluish-green long afterglow luminescence and the adding of Ln ion can obviously strengthen its luminescent intensity as shown from experiment 2 in TABLE 8,there is a sharp difference compared with the comparative sample, a very strong bluish-green afterglow luminescence can be presented ,and its emission spectrum, excitation spectrum are shown in FIG.11(a),(b).

3.When z=0.75, select chemical composition formula $2(Sr_{0.75}Ca_{0.75})O \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3:Eu_{0.004},Ln_{0.02}$ as seen in experiment 7-12 of TABLE 8, the phosphors present greenish—yellow long afterglow luminescence, and the adding of Ln ion can obviously strengthen its luminescent intensity, which can be seen from experiment 8 in TABLE 8, there in an obvious enhancement compared with the comparative sample, its emission spectrum, excitation spectrum are shown FIG.12(a),(b).

TABLE 8

Ex	Chemical composition formula	Relative afterglow intensity		Luminescent color
		10'	60'	
1	$2(Sr_{0.75}Ca_{0.25})O \cdot MgO \cdot 2SiO_2 \cdot 0.01B_2O_3:Eu_{0.01}$	121	162	bluish-green
2	$2(Sr_{0.75}Ca_{0.25})O \cdot MgO \cdot 2SiO_2 \cdot 0.01B_2O_3:Eu_{0.01}Dy_{0.02}$	1758	3874	bluish-green
3	$2(Sr_{0.75}Ca_{0.25})O \cdot MgO \cdot 2SiO_2 \cdot 0.01B_2O_3:Eu_{0.01}Nd_{0.02}$	1121	1671	bluish-green
4	$2(Sr_{0.75}Ca_{0.25})O \cdot MgO \cdot 2SiO_2 \cdot 0.01B_2O_3:Eu_{0.01}Ho_{0.02}$	1023	1642	bluish-green
5	$2(Sr_{0.75}Ca_{0.25})O \cdot MgO \cdot 2SiO_2 \cdot 0.01B_2O_3:Eu_{0.01}Sn_{0.02}$	267	342	bluish-green
6	$2(Sr_{0.75}Ca_{0.25})O \cdot MgO \cdot 2SiO_2 \cdot 0.01B_2O_3:Eu_{0.01}Bi_{0.02}$	323	407	bluish-green
7	$2(Sr_{0.75}Ca_{0.25})O \cdot MgO \cdot 2SiO_2 \cdot 0.01B_2O_3:Eu_{0.01}$	171	303	greenish-yellow
8	$2(Sr_{0.75}Ca_{0.25})O \cdot MgO \cdot 2SiO_2 \cdot 0.01B_2O_3:Eu_{0.01}Dy_{0.02}$	617	1247	greenish-yellow
9	$2(Sr_{0.75}Ca_{0.25})O \cdot MgO \cdot 2SiO_2 \cdot 0.01B_2O_3:Eu_{0.01}Nd_{0.02}$	517	928	greenish-yellow
10	$2(Sr_{0.75}Ca_{0.25})O \cdot MgO \cdot 2SiO_2 \cdot 0.01B_2O_3:Eu_{0.01}Ho_{0.02}$	361	808	greenish-yellow
11	$2(Sr_{0.75}Ca_{0.25})O \cdot MgO \cdot 2SiO_2 \cdot 0.01B_2O_3:Eu_{0.01}Sn_{0.02}$	231	431	greenish-yellow
12	$2(Sr_{0.75}Ca_{0.25})O \cdot MgO \cdot 2SiO_2 \cdot 0.01B_2O_3:Eu_{0.01}Bi_{0.02}$	272	489	greenish-yellow

(5)Other long afterglow luminescent materials

[0051]

1.In the chemical composition formula, when $M=Sr_{1-z}Ca_z$, wherein $0\leq z\leq 1$, M'=Mg, $R=B_2O_3$, a=3, b=1, c=2, d=0.1,that means the formula is $3MO \cdot MgO \cdot 2SiO_2 0.1B_2O_3:Eu_x,Ln_y$, the phosphors display long luminescence from blue to greenish-yellow.

In TABLE 9, M=Sr, Ln=Dy or Nd was selected in experiment 1,the phosphors display blue long afterglow. The emission spectrum, excitation spectrum and x-ray diffraction pattern of $3SrO \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3:Eu_{0.004},Dy_{0.02}$ phosphor are shown in FIG.13 (a),(b) and FIG.14 respectively. The peak of the emission spectrum is 462nm. The dominant compound is $Sr_3MgSi_2O_8$,and the secondary is $Sr_2MgSi_2O_7$, The chemical formula of the phosphor $Sr_3MgSi_2O_8$:Eu,Ln is defined.

In TABLE 9,M=Ca, Ln=Dy or Nd was selected in the experiment 2, the phosphors display light green long afterglow. The emission spectrum excitation spectrum and x-ray diffraction pattern of the $3CaO \cdot MgO\ 2SiO_2:Eu_{0.04},Dy_{0.02}$ phosphor are shown in FIG.15(a), (b) and FIG.16 respectively and the peak of the emission spectrum is 475nm. The dominant compound is $Ca_3MgSi_2O_8$, and the secondary is $Ca_3MgSi_2O_7$.

When $M=Sr_{0.5}Ca_{0.5}$,Ln=Dy or Nd, the phosphors display bluish-green afterglow. The long afterglow property of them is shown in

the experiment 3-1~2 of TABLE 9.

TABLE 9

Experiment	Chemical composition formula	Relative afterglow intensity		Luminescent color
		10'	60'	
1-1	$3SrO \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3:Eu_{0.004}Nd_{0.02}$	211	489	blue
1-2	$3SrO \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3:Eu_{0.004}Dy_{0.02}$	300	579	blue
2-1	$3CaO \cdot MgO \cdot 2SiO_2 0.1B_2O_3:Eu_{0.004}Nd_{0.02}$	31.4	56.1	light green
2-2	$3CaO \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3:Eu_{0.004}Dy_{0.02}$	67.1	146	light green
3-1	$3(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2:0.1B_2O_3:Eu_{0.004}Dy_{0.02}$	173	345	bluish-green
3-2	$3(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2:0.1B_2O_3:Eu_{0.004}Nd_{0.02}$	91	183	bluish-green
Comparative samples	(CaSr)S:Bi	100	100	
	ZnS:Cu	100	100	

2. In the chemical composition formula, when M is $Sr_{1-z}Ca_z$, where $0\leq z\leq 1$, M' is Mg, 0-40% mol of M and/or M' can be partly taken the place by one or more elements from a group consisting of Ba, Zn, Cd, and Be, then the colors of the afterglow are blue, green, yellow etc.

The afterglow colors of the phosphors, in which M mainly consists of Sr, are from blue to blue -green, that is shown in the experiment of 1-1~4 of TABLE 10, the long afterglow property of them is compared with (CaSr)S:Bi; if M mainly consists of Ca or Sr and Ca, the afterglow colors of the phosphors are from green to yellow, that is indicated in the experiment 2-1~4 and 3-1~2 of TABLE 10.The long afterglow property of them is compared with (ZnCd)S:Cu and ZnS:Cu respectively. It is obvious that the long afterglow property of these phosphor is much more superior than that of the comparative samples.

TABLE 10

Experiment	Chemical composition formula	Relative afterglow intensity	
		10'	60'
1-1	$2(Sr_{0.9}Zn_{0.1})O \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3:Eu_{0.004}Dy_{0.02}$	976	1793
1-2	$2SrO \cdot (Mg_{0.9}Zn_{0.1})O \cdot 2SiO_2 \cdot 0.1B_2O_3:Eu_{0.004}Nd_{0.02}$	1170	2104

TABLE 10 (continued)

Experiment	Chemical composition formula	Relative afterglow intensity	
		10'	60'
1-3	$2SrO \cdot (Mg_{0.9}Ba_{0.1})O \cdot 2SiO_2 \cdot 0.1B_2O_3:Eu_{0.004}Dy_{0.02}$	836	1706
1-4	$2(Sr_{0.9}Cd_{0.1})O \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3:Eu_{0.004}Dy_{0.02}$	1031	1842
2-1	$2(Ca_{0.9}Zn_{0.1})O \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3:Eu_{0.004}Dy_{0.02}$	635	784
2-2	$2CaO \cdot (Mg_{0.9}Zn_{0.1})O \cdot 2SiO_2 \cdot 0.1B_2O_3:Eu_{0.004}Dy_{0.02}$	703	802
2-3	$2(Ca_{0.95}Ba_{0.05})O\ MgO \cdot 2SiO_2 \cdot 0.1B_2O_3:Eu_{0.004}Nd_{0.02}$	507	769
2-4	$2CaO \cdot (Mg_{0.9}Be_{0.1})O \cdot 2SiO_2 \cdot 0.1B_2O_3:Eu_{0.004}Dy_{0.02}$	603	726
3-1	$2(Sr_{0.495}Ca_{0.495}Zn_{0.05})O \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3:Eu_{0.004}Dy_{0.02}$	1083	2835
3-2	$2(Sr_{0.5}Ca_{0.5})O \cdot (Mg_{0.9}Ba_{0.1})O \cdot 2SiO_2 \cdot 0.1B_2O_3:Eu_{0.004}Dy_{0.02}$	1017	2786
Comparative samples	(CaSr)S:Bi	100	100
	(ZnCd)S:Cu	100	100
	ZnS:Cu	100	100

3. When M=Ba, a=5, b=0, c=8, R=B_2O_3, d=0.1, the formula of the phosphors is $5BaO \cdot 8SiO_2\ 0.1B_2O_3:Eu_x,Ln_y$ the synthesized phosphor, in which x=0.01, Ln=Dy, y=0.02 shows light green luminescence, and the dominant compound is $Ba_5Si_8O_{31}$, the emission spectrum and excitation spectrum are shown in FIG. 17(a), (b), TABLE 11 shows its relative persistence property. Ba being partly replaced by one or more elements from a group consisting of Ca, Sr, Mg, Zn, Cd and Be, the phosphors display persistence luminescence too.

TABLE 11

Experiment	Chemical composition formula	Relative afterglow intensity	
		10'	60'
1-1	$Ba_5Si_8O_{31}$:Eu,Dy	87.4	100
comparative sample	ZnS:Cu	100	100

4. When M=Zn, R=B_2O_3, a=2, b=0, c=1, d=0.1, Ln=Dy and Mn, x=0.01, y=0.02, the synthesized phosphor shows light green afterglow and the main compound is Zn_2SiO_4. The decay property is shown in TABLE 12. Zn being partly replaced by one or more elements from a group consisting of Ca , Sr, Mg, Ba, Cd and Be the phosphor shows decay luminescence too.

TABLE 12

Experiment	Chemical composition formula	Relative afterglow	
		10'	60'
1-1	Zn_2SiO_4:Eu,Dy,Mn	32.6	95.8
Comparative sample	ZnS:Cu	100	100

[0052] In this invention it is also found that put other additives (0-15% weight of the raw material) to the raw material can more or less improve the long afterglow intensity of phosphor and the quality of the synthesized product, but didn't change its dominant crystal structure and main compound, the influence of the additives on the afterglow property of the greenish—yellow phosphors is indicated in TABLE 13.

[0053] In TABLE 13 the greenish-yellow phosphor is selected wherein $M=Sr_{0.3}Ca_{0.7}$,M'=M,R=B_3O_3,Ln=Dy,a=2.5,b=1.2,c=2.5,d=0.1,x=0.02,y=0.1

TABLE 13

Ex	Chemical composition formula	Added compound	Mol	Relative afterglow intensity	
				10'	60'
1	$2.5(Sr_{0.3}Ca_{0.7}O) \cdot 1.2MgO \cdot 2.5SiO_2 \cdot 0.1B_2O_3$:Eu$_{0.02}Dy_{0.1}$	0	0	643	1374
2	$2.5(Sr_{0.3}Ca_{0.7}O) \cdot 1.2MgO \cdot 2.5SiO_2 \cdot 0.1B_2O_3$:Eu$_{0.02}Dy_{0.1}$	NH_4Cl	0.1	684	1427
3	$2.5(Sr_{0.3}Ca_{0.7}O) \cdot 1.2MgO \cdot 2.5SiO_2 \cdot 0.1B_2O_3$:Eu$_{0.02}Dy_{0.1}$	NH_4F	0.1	672	1395
4	$2.5(Sr_{0.3}Ca_{0.7}O) \cdot 1.2MgO \cdot 2.5SiO_2 0.1B_2O_3$:Eu$_{0.02}Dy_{0.1}$	Li_2CO_3	0.05	693	1432
5	$2.5(Sr_{0.3}Ca_{0.7}O) \cdot 1.2MgO \cdot 2.5SiO_2 \cdot 0.1B_2O_3$:Eu$_{0.02}Dy_{0.1}$	SrF_2	0.1	675	1398
6	$2.5(Sr_{0.3}Ca_{0.7}O) \cdot 1.2MgO \cdot 2.5SiO_2 \cdot 0.1B_2O_3$:Eu$_{0.02}Dy_{0.1}$	CaF_2	0.1	663	1388
7	$2.5(Sr_{0.3},Ca_{0.7}O) \cdot 1.2MgO \cdot 2.5SiO_2 \cdot 0.1B_2O_3$:Eu$_{0.02}Dy_{0.1}$	$CaSO_4$	0.1	670	1391
8	$2.5(Sr_{0.3}Ca_{0.7}O) \cdot 1.2MgO \cdot 2.5SiO_2 \cdot 0.1B_2O_3$:Eu$_{0.02}Dy_{0.1}$	$SrSO_4$	0.1	675	1382
9	$2.5(Sr_{0.3}Ca_{0.7}O) \cdot 1.2MgO \cdot 2.5SiO_2 \cdot 0.1B_2O_3$:Eu$_{0.02}Dy_{0.1}$	$SrHPO_4$	0.1	682	1407
10	$2.5(Sr_{0.3}Ca_{0.7}O) \cdot 1.2MgO \cdot 2.5SiO_2 \cdot 0.1B_2O_3$:Eu$_{0.02}Dy_{0.1}$	$CaHPO_4$	0.1	667	1379

[0054] In other chemical formula more or less influence of these additives on the afterglow property is found as well.

[0055] The phosphors of this invention have good water resistance property and better stability. In the same condition, putting the long afterglow phosphor of aluminate and a long afterglow silicate phosphor of this invention into water respectively it is found that the aluminate's phosphor decomposed after three days and decomposed entirely after a week and losing the luminescent property ,but the silicate's phosphor didn't decompose even after three months . The afterglow property still existed.

[0056] This invention have the following outstanding features compared with the present technology:

(1)Inventing a new series of long afterglow phosphors with silicate as the dominant host lattice that possesses the fairly good chemical stability and water resistance property, and changeable afterglow colors : blue bluish—green, green, greenish-yellow and yellow.

(2)Inventing of some ions can enhance the luminescence of the Eu^{2+} and improve the afterglow luminescent properties.

(3)Adding of boron and phosphors compound can make further improvement on the luminescent properties .

[0057] The invention is described in detail hereafter by referring to the examples and figures.

EXAMPLES

Example 1: $2SrO \cdot MgO \cdot 2SiO_2 \cdot 0.1B_2O_3$:$Eu_{0.004}$ phosphor's synthesis and analysis results

[0058] Match of the raw materials:

Element	Mol	Raw Material	Weight
Sr	1.996	$SrCO_3$	294.6g
Mg	1	$4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$	97.1g
Si	2	SiO_2	120g
B	0.2	B_2O_3	6.96g
Eu	0.004	Eu_2O_3	0.704g

[0059] The above raw material was ground into fine and mixed homogenously, ten placed in alumina crucible and fired in the furnace which full of $NH_3(g)$ atmosphere at 1350 °C for 3 hrs, after that cooled down and smashed the fired phosphor, finally sifted it out by the sieve of 100 mesh.

[0060] The appearance of this phosphor is greyish white, after irradiated under sun light it can present blue afterglow color in dark; measured the phosphor's luminescent afterglow intensity, show in experiment 1-4 in TABLE 4, FIG. 1 (a), (b) and figure 2 are the example phosphor's emission spectrum, excitation spectrum and x-ray diffraction pattern respectively, according to its x-ray diffraction pattern, its crystal structure, is akermanite and its compound is $Sr_2MgSi_2O_7$, the phosphor's chemical formula $Sr_2MgSi_2O_7$:Eu is defined.

Example 2: $2SrO \cdot MgO \cdot 2SiO_2 \cdot 0.1B_3O_3:Eu_{0.004},Dy_{0.04}$ phosphor's synthesis and analysis results

[0061] Match of the raw materials:

Element	Mol	Raw Material	Weight
Sr	1.96	$SrCO_3$	289.3g
Mg	0.996	$4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$	96.7g
Si	2	SiO_2	120g
B	0.2	H_2BO_3	13.56g
Eu	0.004	Eu_2O_3	0.704g
Dy	0.04	Dy_2O_3	7.46g

[0062] The above raw material is ground into fine and mixed homogenously in alcohol solution , after baking, placed in alumina crucible, and fired in a high temperature furnace which full of $NH_3(g)$ atmosphere at 1350 °C for 3 hrs, after that cooled down, smashed the fired phosphor, finally sifted it out by the sieve of 100 mesh,

[0063] The appearance of this phosphor is greyish white, after irradiated under fluorescent lamp, it displays very strong blue afterglow in dark, the phosphor's relative luminescent intensity shown as experiment 3-4 in TABLE4, its intensity is obviously higher than that of example 1; besides, the material's afterglow time is long, see figure 7; figure3(a)(b) are phosphor's emission spectrum and excitation spectrum respectively ;the phosphor's crystal structure and main compound same as example 1,the phosphor's chemical formula $Sr_2MgSi_2O_7$:Eu,Dy is defined.

Example 3: $SrO \cdot 3MgO \cdot 2SiO_2 \cdot 0.05P_2O_s:Eu_{0.004},Nd_{0.01}$ phosphor's synthesis

[0064] Match of the raw materials:

Element	Mol	Raw Material	Weight
Sr	0.993	$SrCO_3$	146.6g

(continued)

Element	Mol	Raw Material	Weight
Mg	2.993	$4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$	290.6g
Si	2	SiO_2	120g
P	0.1	$(NH_4)_2HPO_4$	13.2g
Eu	0.004	Eu_2O_3	0.704g
Nd	0.1	Nd_2O_3	1.68g

[0065] The above raw material is ground into fine and mixed homogeneously in acetone solution, after baking, placed in alumina crucible, and fired in a furnace which full of $H_2(g)$ atmosphere at 1350 °C for 3 hrs, after that cooled and smashed the fired phosphor, finally sifted it out by the sieve of 100mesh.

[0066] This phosphor can display stronger blue afterglow after irradiated under ultraviolet lamp, analyzed from x-ray diffraction pattern, its dominant compound is Sr_2MgSiO_7 and Mg_2SiO_4, the phosphor's chemical composition formula $SrO \cdot 3MgO \cdot 2SiO_2 \cdot 0.05P_2O_5$:Eu,Nd is defined.

[0067] Example 4: $2CaO \cdot MgO \cdot 2SiO_2 \cdot 0.15B_2O_3$;$Eu_{0.004}$,$Dy_{0.05}$ phosphor's synthesis and analysis results.

[0068] Match of the raw materials:

Element	Mol	Raw Material	Weight
Ca	1.946	$CaCO_3$	194.6g
Mg	1	$4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$	97.1g
Si	2	SiO_2	120g
B	0.3	H_3BO_3	18.84g
Eu	0.004	Eu_2O_3	0.764g
Dy	0.05	Dy_2O_3	9.325g

[0069] The above raw material is ground into fine and mixed homogeneously, then placed in alumina crucible fired in a high temperature furnace which full of 30% $H_2(g)$+70% $N_2(g)$ atmosphere at 1320 °C for 5hrs,after that cooled and smashed the fired phosphor, finally sifted it out by the sieve of 100mesh.

[0070] The appearance of this phosphor is light yellow, after irradiated under fluorescent lamp, it can presents very strong yellow afterglow in dark; the phosphor's relative luminescent intensity shown as experiment 2-3 in TABLE 5, which is obviously stronger than that of experiment 1-4 in TABLE 5, its emission spectrum, excitation spectrum are shown in FIG.5(a),(b);the phosphor's afterglow time is long ,FIG. 7 is phosphor's afterglow characteristic curve, the phosphors's main crystal structure is akermamite and its compound is $Ca_2MgSi_2O_7$, see FIG. 6, so the phosphor's chemical formula is defined as $Ca_2MgSi_2O_7$:Eu,Dy.

Example 5: $1.5CaO \cdot 3MgO \cdot 2SiO_2 \cdot 0.15B_2O_3$:$Eu_{0.004}$,$Ho_{0.08}$ phosphor's synthesis.

[0071] Match of the raw materials:

Element	Mol	Raw Material	Weight
Ca	1.5	$CaCO_3$	150g
Mg	3	$4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$	291.3g
Si	2	H_2SiO_3	156g
B	0.15	B_2O_3	10.44g

(continued)

Element	Mol	Raw Material	Weight
Eu	0.004	Eu_2O_3	0.704g
Ho	0.08	Ho_2O_3	15.1g

[0072] The synthesis method of this phosphor is the same as example 1, after irradiated under ultraviolet lamp, this phosphor displays yellow afterglow, according to the x-ray diffraction pattern, its compounds is $Ca_2MgSi_2O_7$,$CaMgSiO_4$ and $Ca_3Si_2O_7$ so the phosphor's chemical composition formula $1.5CaO \cdot 3MgO \cdot 2SiO_2 \cdot 0.15B_2O_3$:Eu,Ho is defined.

Example 6:$2(Sr_{0.5}Ca_{0.5})O \cdot MgO \cdot 2SiO_2 \cdot 0.05B_2O_3$:$Eu_{0.005}$,$Dy_{0.08}$ phosphor's synthesis and analysis results

[0073] Match of the raw materials:

Element	Mol	Raw Material	Weight
Sr	1	$SrCO_3$	147.6g
Ca	1	$CaCO_3$	100g
Mg	1	$4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$	97.1g
Si	2	SiO_2	120g
B	0.1	H_3BO_3	6.28g
Eu	0.005	Eu_2O_3	0.88g
Dy	0.08	Dy_2O_3	14.92g

[0074] The above raw material is ground and mixed homogeneously, placed in alumina crucible, fired for 3 hrs at 1300 °C in NH_3(g) atmosphere, after that cooled down and smashed the fired phosphor, finally sifted it out by the sieve of 100mesh.

[0075] The appearance of this phosphor is light green, after irradiated under fluorescent lamp it displays strong green afterglow. This phosphor's relative afterglow intensity is shown in TABLE 6. The emission spectrum, excitation spectrum and x-ray diffraction pattern of this phosphor are shown in FIG.8(a),(b) and FIG.9 respectively. The phosphor's afterglow time is long and FIG. 10 is the afterglow characteristics curve. Its chemical formula $(Sr_{0.5}\ Ca_{0.5})_2MgSi_2O_7$:Eu,Dy is defined.

Example 7. $2(Sr_{0.25}Ca_{0.75})O \cdot MgO \cdot 2.3SiO_2 \cdot 0.05P_2O_5$:$Eu_{0.01}$,$Nd_{0.02}$ phosophor's synthesis

[0076] Match of the raw material:

Element	Mol	Raw Material	Weight
Sr	0.5	$Sr(NO_3)_2$	105.8g
Ca	1.5	$Ca(NO_3)_2 \cdot 4H_2O$	354g
Mg	1	$Mg(NO_3)_2 \cdot 6H_2O$	256.4g
Si	2.3	silica gel	138g
P	0.1	$NH_4H_2PO_4$	11.5g
Eu	0.01	Eu_2O_3	1.76g
Nd	0.02	Nd_2O_3	3.36g

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[0077] The synthesis method of this phosphor is the same as described in example 1.

[0078] This phosphor displays greenish-yellow afterglow after irradiated under fluorescent lamp. The x-ray diffraction pattern of this phosphor is similar to FIG.9, so it can be deduced that its compound is $(Sr_{0.25}Ca_{0.75})_2MgSi_2O_7$, its chemical formula $(Sr_{0.25}Ca_{0.75})_2MgSi_2O_7$: Eu,Nd. is defined.

Example 8. $3SrO \cdot MgO \cdot 2SiO_2:Eu_{0.001},Ho_{0.08}$ phosphor's synthesis

[0079] Match of the raw material:

Element	Mol	Raw Material	Weight
Sr	3	$Sr(NO_3)_2$	634.8g
Mg	1	MgO	40.3g
Si	2	H_2SiO_3	156g
Eu	0.01	Eu_2O_3	1.76g
Ho	0.08	Ho_2O_3	15.1g

[0080] The synthesis method of this phosphor is the same as described in example 1.

[0081] This phosphor displays blue afterglow after irradiated under sunlight, its dominant compound is $Sr_3MgSi_2O_8$, the secondary is $Sr_2MgSi_2O_7$, so the chemical formula $Sr_3MgSi_2O_8$:Eu,Ho is defined.

Example 9. $2(Sr_{0.6}Ca_{0.4})O \cdot (Mg_{0.8}Cd_{0.2})O \cdot 2.5SiO_2 \cdot 0.1B_2O_3:Eu_{0.001}\ Dy_{0.02}Bi_{0.01}$ phosphor's synthesis.

[0082] Match of the raw material:

Element	Mol	Raw Material	Weight
Sr	1.3	$SrCO_3$	177.1g
Ca	0.8	$CaCO_3$	80g
Mg	0.8	$4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$	77.7g
Cd	0.2	CdO	25.7g
Si	2.5	SiO_2	150g
B	0.2	B_2O_3	6.96g
Eu	0.01	Eu_2O_3	1.76g
Dy	0.02	Dy_2O_3	3.73g
Bi	0.01	Bi_2O_3	2.33g

[0083] Doped 5% NH_4Cl by weight of the raw material, grinding and mixing them together, then firing them as example 1.

[0084] The fired phosphor displays strong bluish-green afterglow after irradiated under sunlight.

Example 10. $5BaO \cdot 8SiO_2 \cdot 0.1B_2O_3:Eu_{0.01}Dy_{0.02}$ phosphor's synthesis

[0085] Match of the raw material:

Element	Mol	Raw Material	Weight
Ba	5	$BaCO_3$	985g
Si	8	SiO_3	480g
B	0.2	B_2O_3	6.96g
Eu	0.01	Eu_2O_3	1.76g
Dy	0.02	Dy_2O_3	3.73g

[0086] The synthesis method of this phosphor is the same described in example 1, after irradiated under sunlight this phosphor displays light green persistence, its compound is $Ba_5Si_8O_{21}$ and so the chemical formula $Ba_5Si_8O_{21}$:Eu,Dy is defined.

INDUSTRY APPLICATION

[0087] The products in this invention can be widely used in all kinds of long afterglow product as indicators or ornaments in dark environment, combined with paint; plastics; printing ink; rubber etc., this series of luminescent materials has good effect in architecture , traffic, decoration, watch and clock dials, fishing tackles, toys and other goods for daily use, it's specially suitable for the production of long afterglow safety product, such as warning, mandatory and escape-route signs.

Claims

1. A long afterglow luminescent material, characterized in that it is mainly composed of silicates with activators; the main chemical composition formula is: $aMO \cdot bM'O \cdot cSiO_2 \cdot dR:Eu_x,Ln_y$ (1)
wherein M represents one or more elements selected from a group consisting of Sr,Ca,Ba and Zn; M' represents one or more elements selected from a group consisting of Mg, Cd and Be; R represents one or two components selected from B_2O_3 and P_2O_5; Ln represents one or more elements selected from a group consisting of Nd, Dy, Ho, Tm, La, Pr, Tb, Ce, Mn, Bi, Sn and Sb; a, b, c, d, x and y represents mole coefficients,
wherein $0.6 \le a \le 6$, $0 \le b \le 5$, $1 \le c \le 9$, $0 \le d \le 0.7$, $0.00001 \le x \le 0.2$, and $0 \le y \le 0.3$; said luminescent materials can give an emission spectrum of 420-650nm when excited by short wavelength light of 250-500nm, whose peak position of emission spectrum is 450-580nm,and the long afterglow luminescent color is blue, bluish-green, green, greenish-yellow or yellow.

2. A long afterglow luminescent material as claimed in claim 1,characterized in that M represents one or two elements selected from Sr and Ca; M' represents Mg; R represent one or two components selected from B_2O_3 and P_2O_5; Ln represents one or more elements selected from a group consisting of Nd, Dy, Ho, Bi and Sn, wherein $0.6 \le a \le 4$, $0.6 \le b \le 4$, $1 \le c \le 5$ and $0 < d \le 0.4$.

3. A long afterglow luminescent material as claimed in claim 2, characterized in that 0-40% mole of the elements M and/or M' can be replaced by one or more elements selected from a group consisting of Ba, Zn, Cd and Be.

4. A long afterglow luminescent material as claimed in claim 1 or claim 2, characterized in that main matrix compound of the luminescent material is: $M_2MgSi_2O_7$ or $M_3MgSi_2O_8$,wherein M represents $Sr_{1-z}Ca_z$,$0 \le z \le 1$.

5. A long afterglow luminescent material as claimed in claim 1 or claim 2, characterized in that main chemical formula of the luminescent material is: $M_2MgSi_2O_7$:Eu,Ln or M3MgSi2O8:Eu,Ln, wherein M represents $Sr_{1-z}Ca_z$,$0 \le z \le 1$.

6. A long afterglow luminescent material as claimed in claim 1 or claim 2, characterized in that main chemical formula of the luminescent material is: $M_2MgSi_2O_7$:Eu,Ln or $M_3MgSi_2O_8$:Eu,Ln, wherein M represents $Sr_{1-z}Ca_z$, $0 \le z \le 1$,Ln represents one or more elements selected from a group consisting of Nd, Dy, Ho, Sn, and Bi.

7. A long afterglow luminescent material as claimed in claim 1, characterized in that main chemical formula of the luminescent material is $Ba_5Si_8O_{21}$: Eu, Dy.

8. A long afterglow luminescent material as claimed in claim 1,characterized in that main chemical formula of the luminescent material is Zn_2SiO_4: Eu, Dy, Mn.

9. A method of manufacturing the long afterglow luminescent material as claimed in claim 1, characterized in that mole proportion of elements in the raw material used to produce the luminescent material are as follows:

M: 0.6-6 R: 0-0.7 in terms of B_2O_3 or P_2O_5
M': 0-5 Eu: 0.00001-0.2
Si:1-9 Ln:0-0.3

wherein

M represents one or more elements selected from a group consisting of Sr, Ca, Ba and Zn,;
M' represents one or more elements selected from a group consisting of Mg, Cd and Be;
R represents one or two elements selected from B and P;
Ln represents one or more elements selected from a group consisting of Nd, Dy, Ho, Tm, La, Pr, Tb, Ce, Mn, Bi, Sn and Sb;

Wherein M, M', Ln and Eu can be incorporated in the raw materials in the form of carbonate, sulphate, nitrate, phosphate, borate, aectate, oxalate, citrate, oxide, hydroxide or halogenide of the elements or their mixture; Si can be added in the form of SiO_2, silicic acid, silica gel or silicate; R can be added in the form of any compounds containing B or P, with the proviso that such compounds can form B_2O_3 or P_2O_5 in a subsequent sintering procedure; the method comprises the following steps: the raw materials of M, M', Ln, Eu, Si and R are weighed, ground and mixed homogeneously, then the mixture is sintered at a temperature between 1100-1400°C for a period about 2 to 50 hours under a reducing atmosphere, finally, the fired mixture is milled and sifted into desired particle size.

10. The method of manufacturing the long afterglow luminescent material as claimed in claim 9, characterized in that the reducing atmosphere in is selected from H_2, NH_3, N_2+H_2, or carbon powder.

11. The method of manufacturing the long afterglow luminescent material as claimed in claim 9, characterized in that NH_4Cl, NH_4F, Li_2CO_3, SrF_2, CaF_2, $CaSO_4$, $SrSO_4$, $SrHPO_4$ or $CaHPO_4$ which amounts to 0-15% by weight of raw material can be added to the mixed raw material to participate in solid-phase reaction.

FIG.1

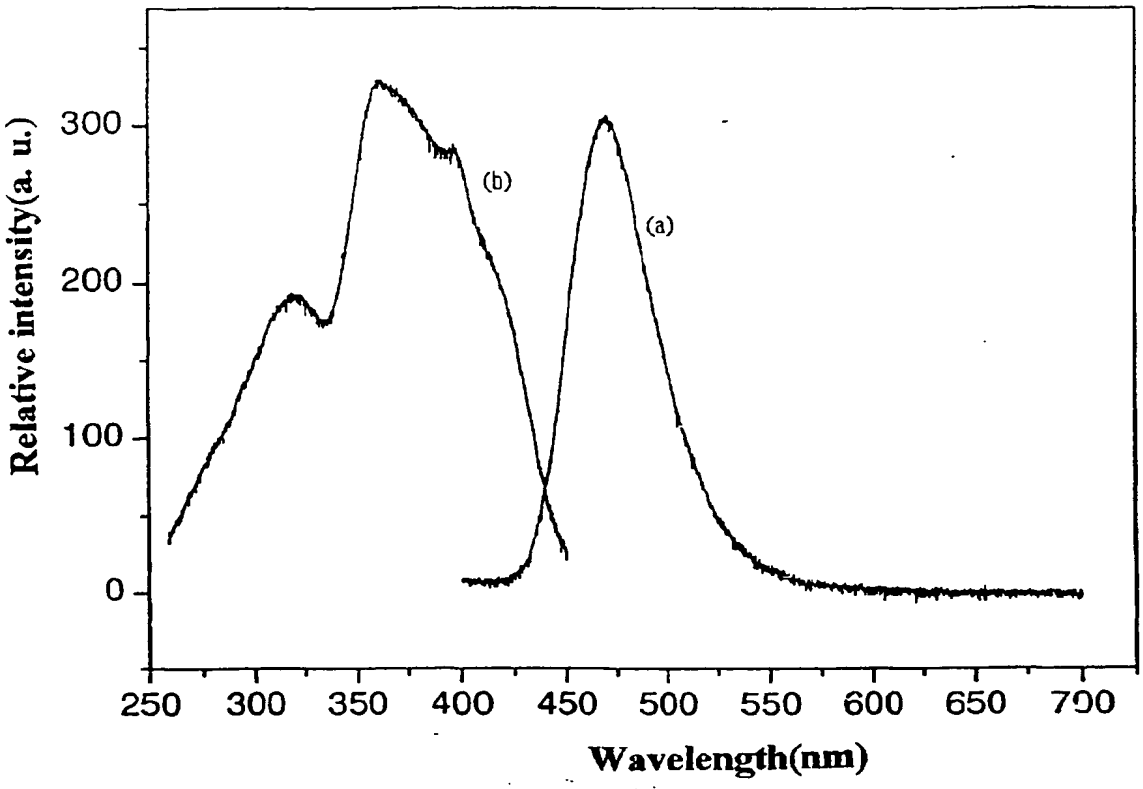
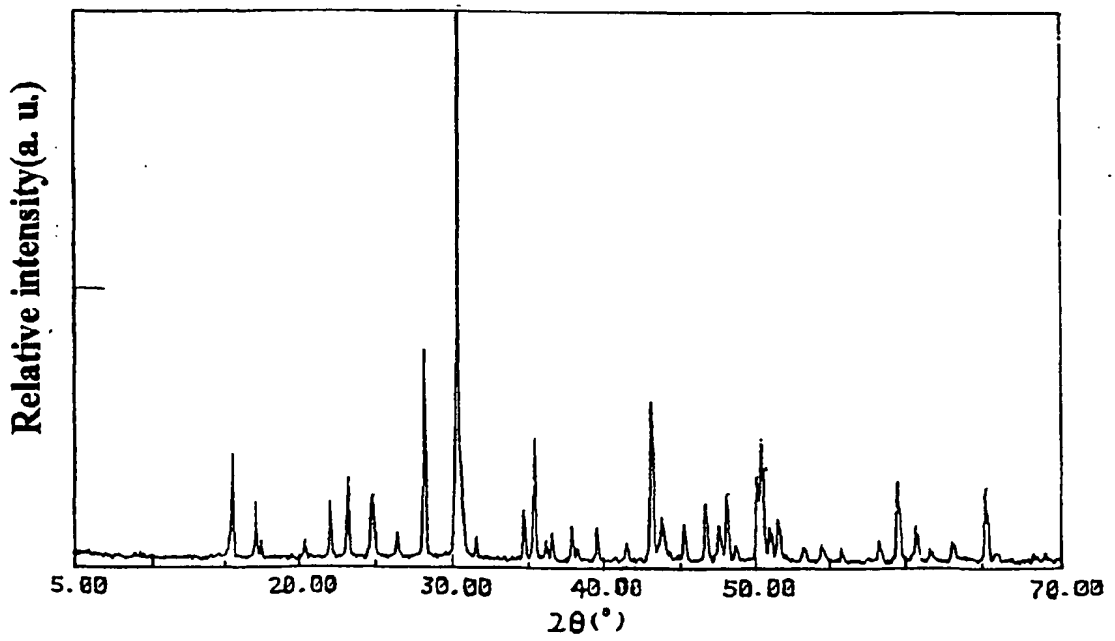

Relative intensity(a. u.)
300
200
100
0
(b)
(a)
250
300
350
400
450
500
550
600
650
700
Wavelength(nm)

FIG.2


Relative intensity(a. u.)
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30.00
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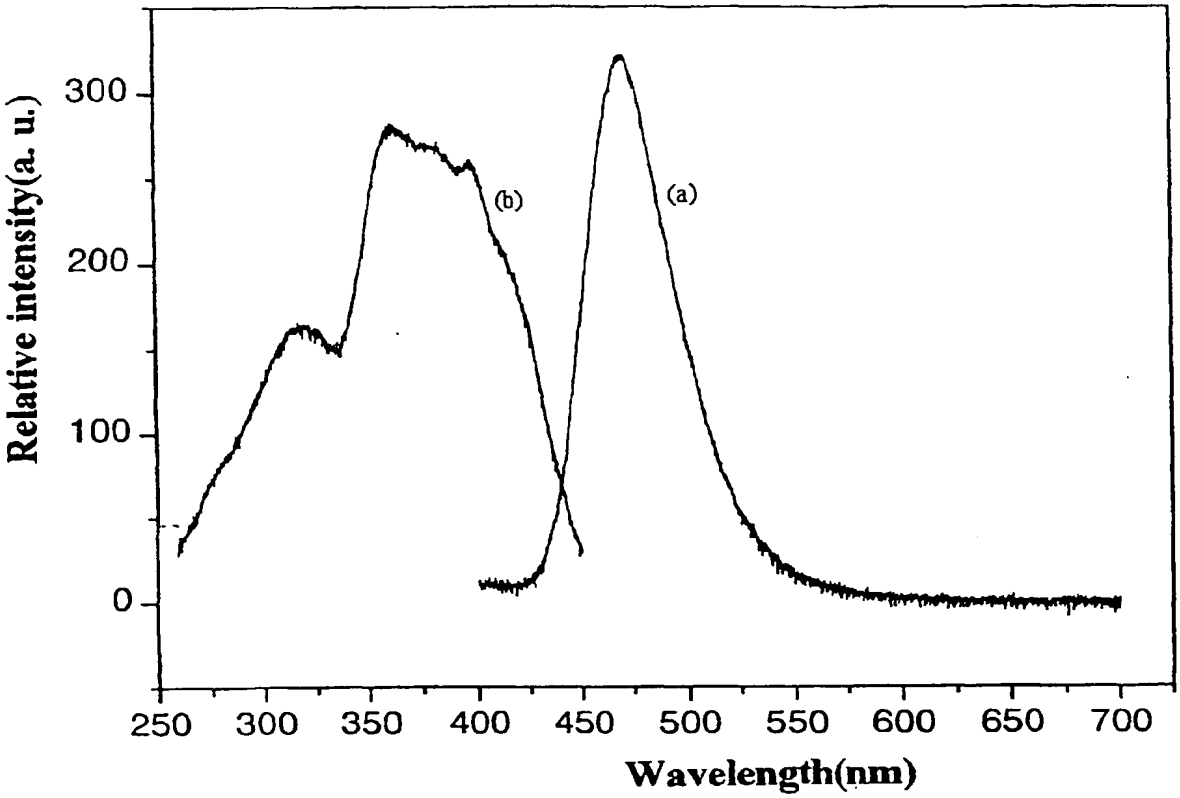
2θ(°)

FIG.3


Relative intensity(a. u.)
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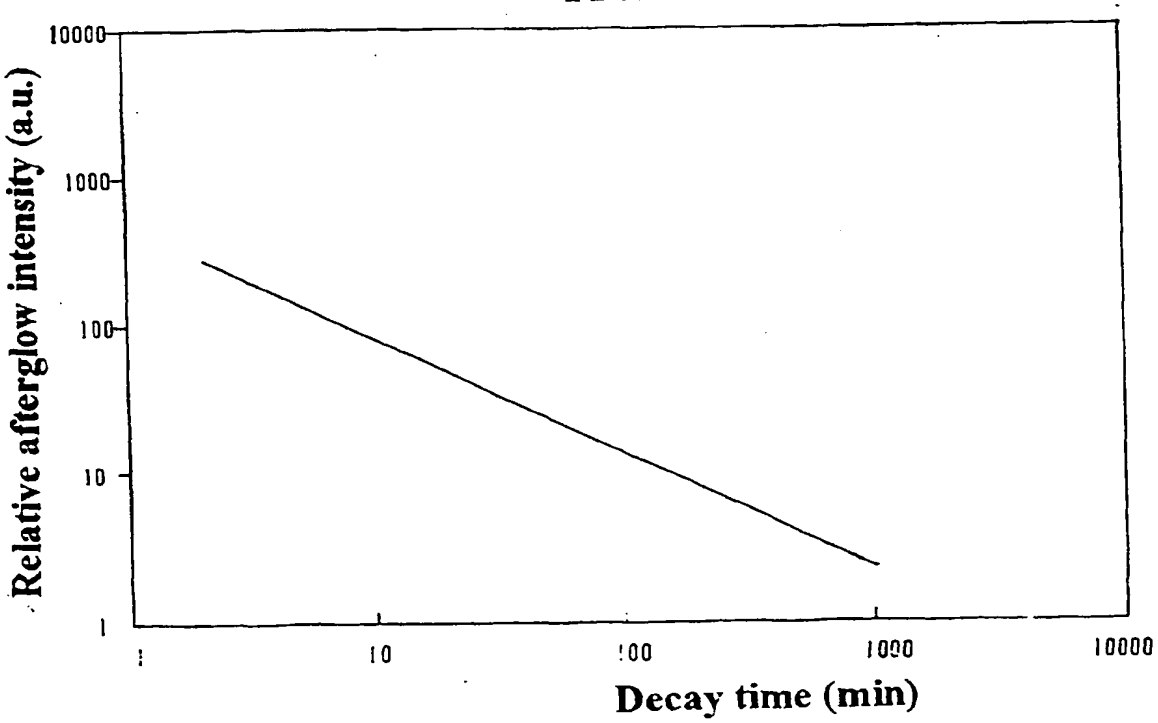
200
100
0
(b)
(a)
250
300
350
400
450
500
550
600
650
700
Wavelength(nm)

FIG.4


Relative afterglow intensity (a.u.)
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1000
100
10
1
1
10
100
1000
10000
Decay time (min)

FIG.5

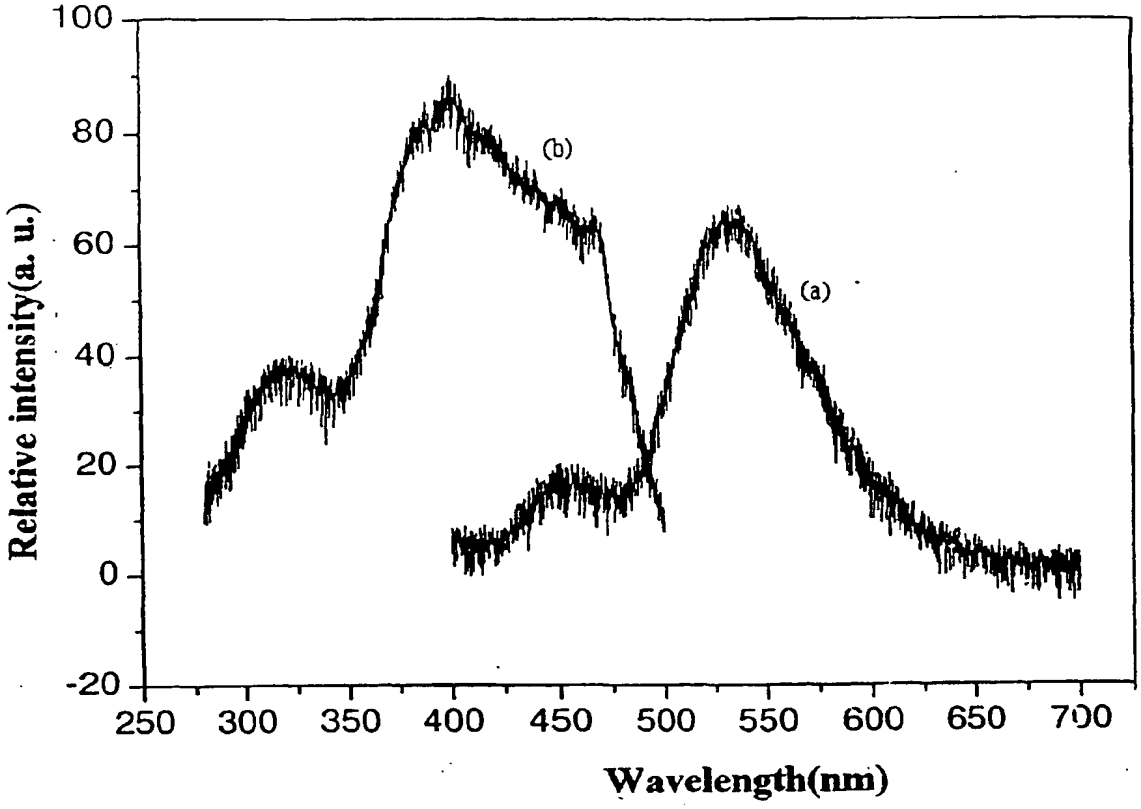
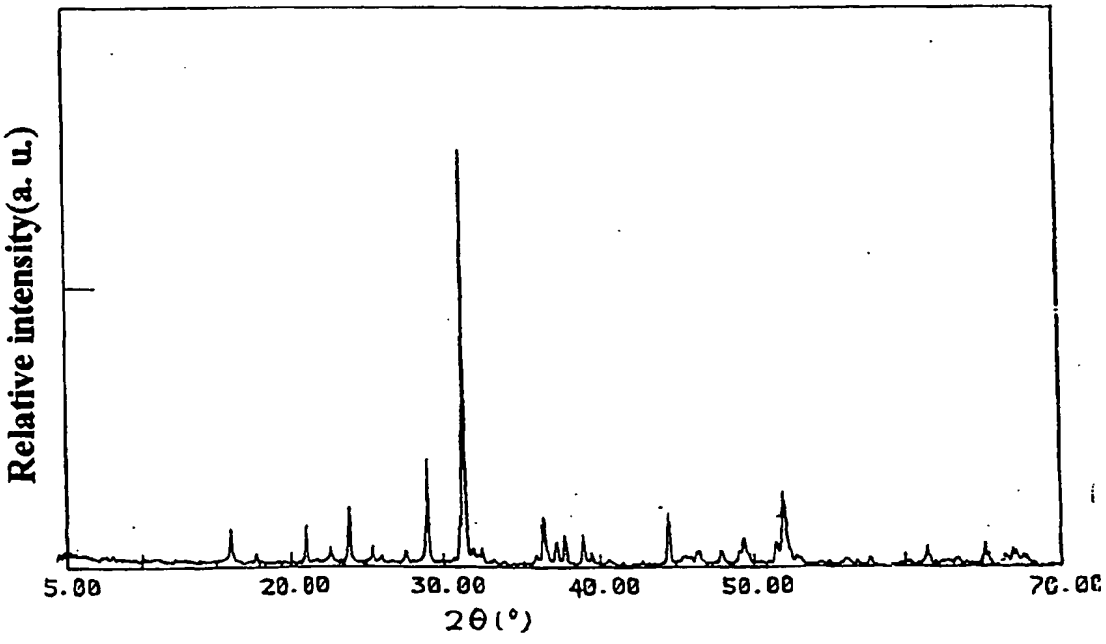

100
80
60
40
20
0
-20
250
300
350
400
450
500
550
600
650
700
Relative intensity(a. u.)
Wavelength(nm)
(b)
(a)

FIG.6


Relative intensity(a. u.)
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50.00
2θ(°)

FIG.7

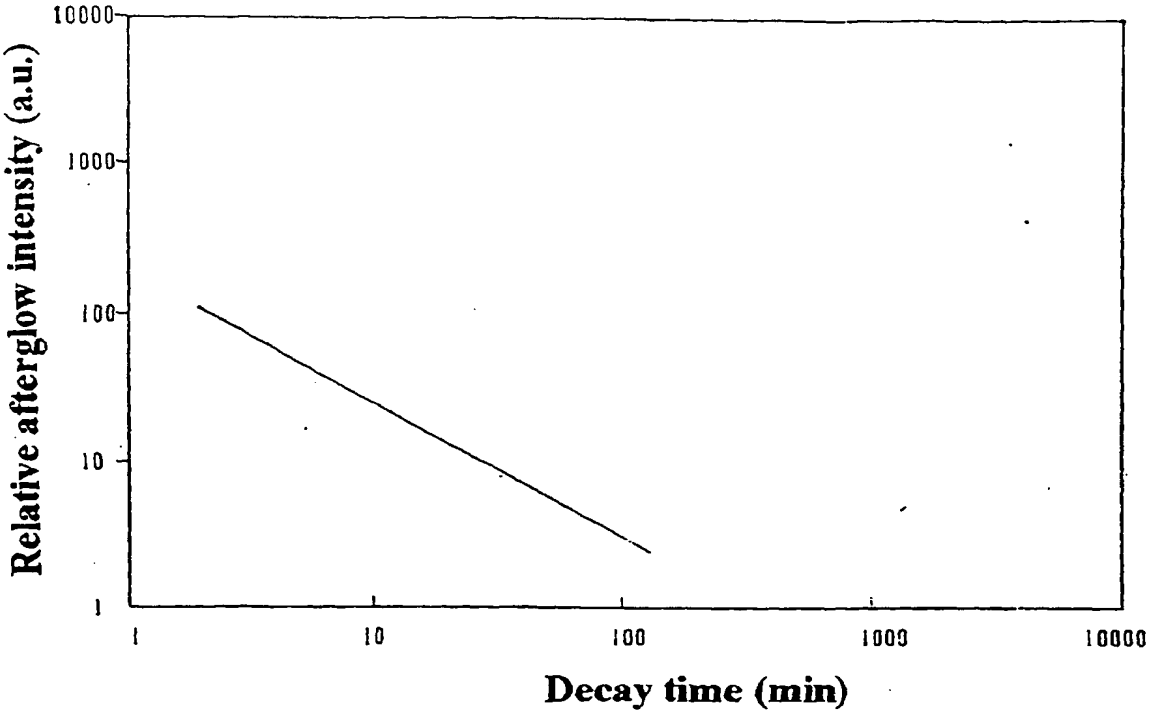


FIG.8

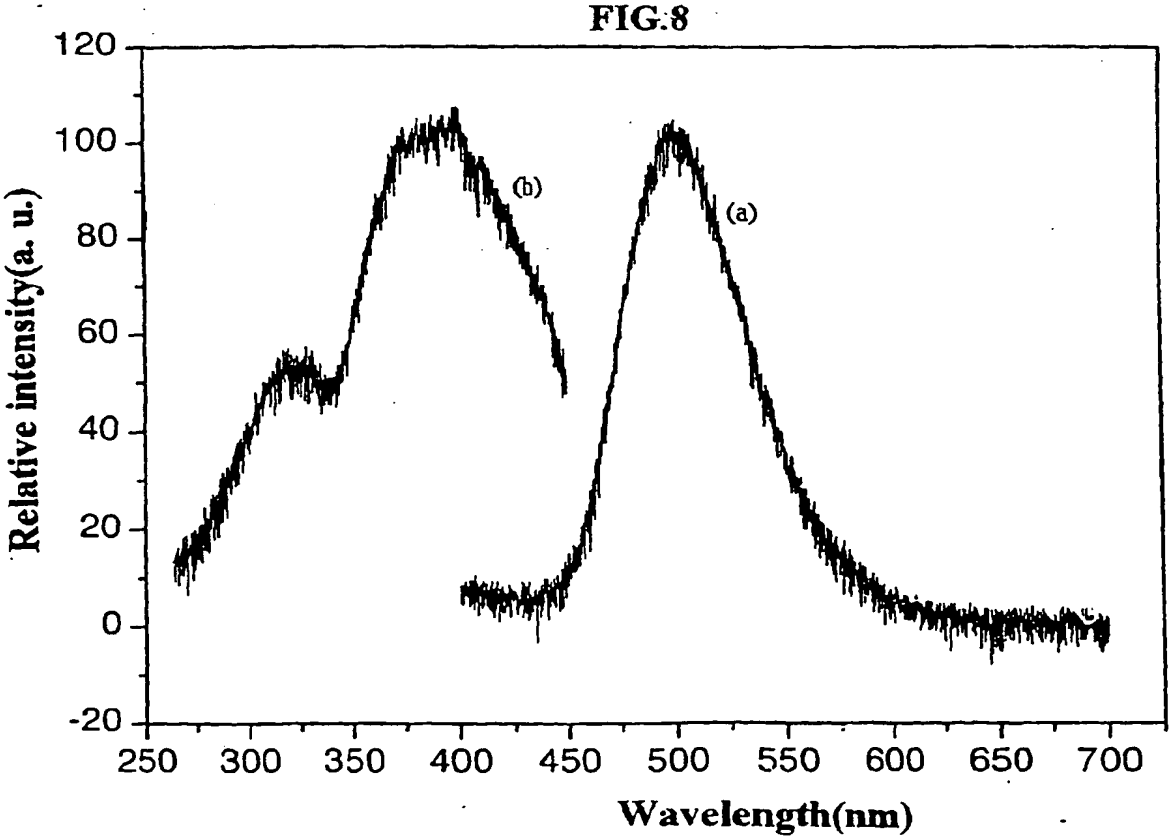


FIG.9

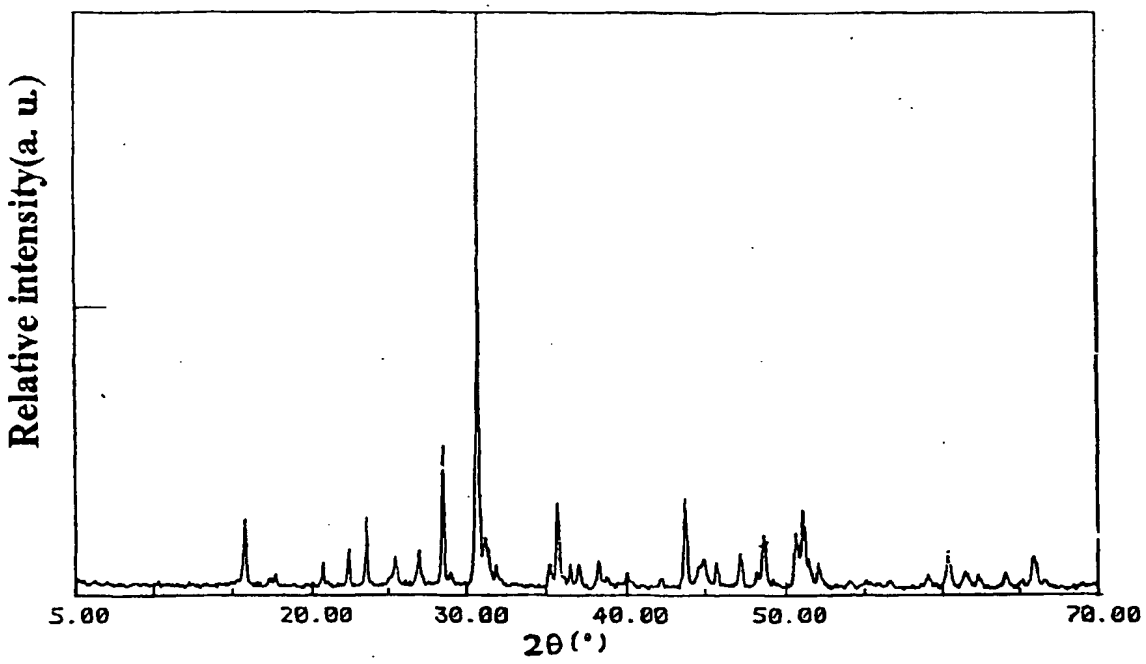


FIG.10

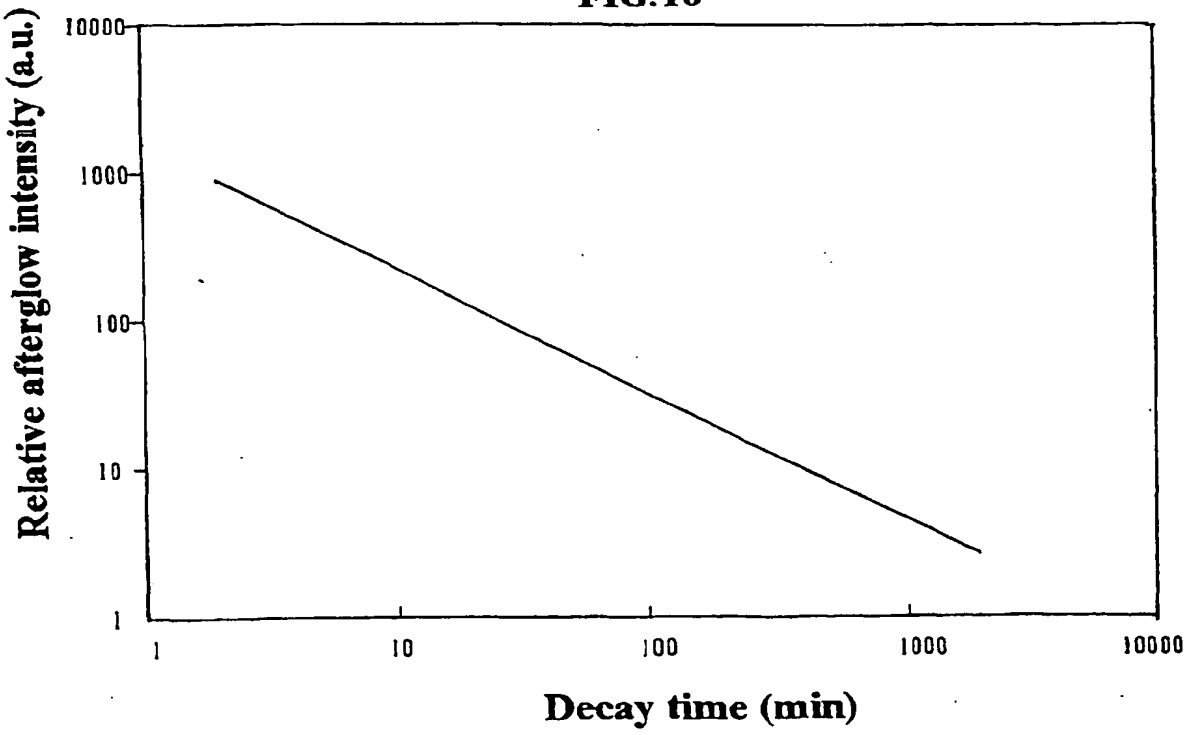


FIG.11

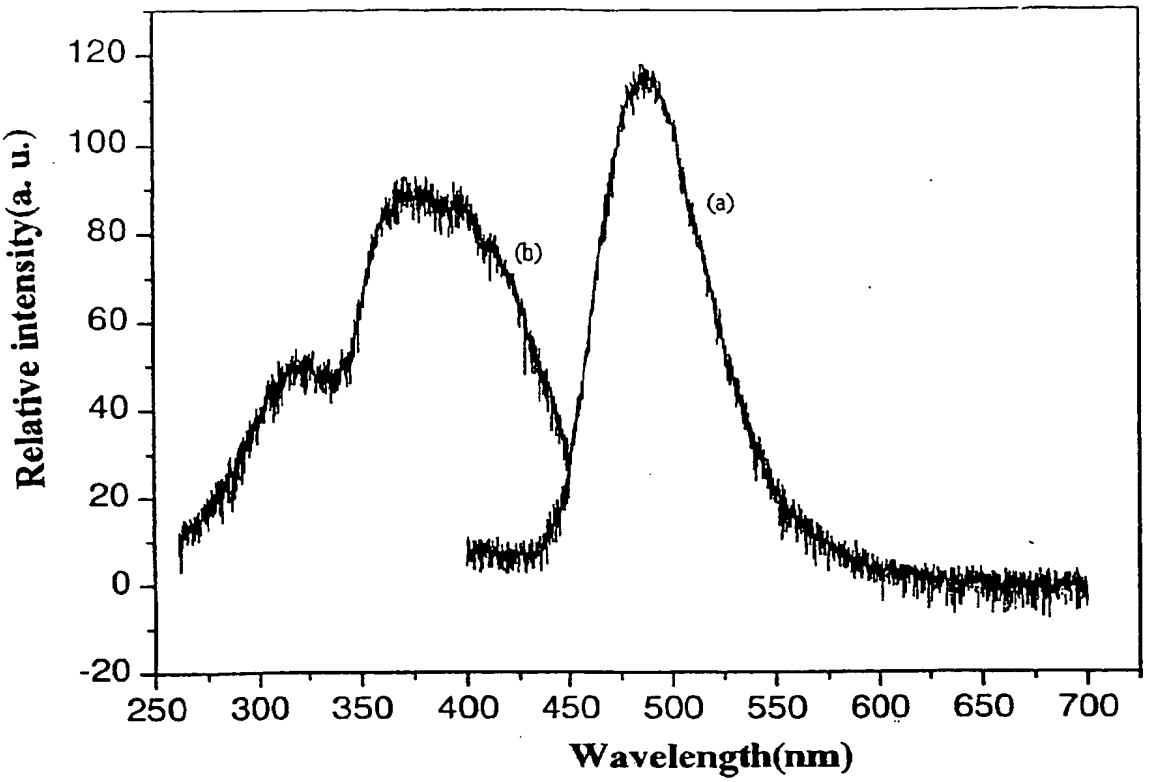


FIG.12

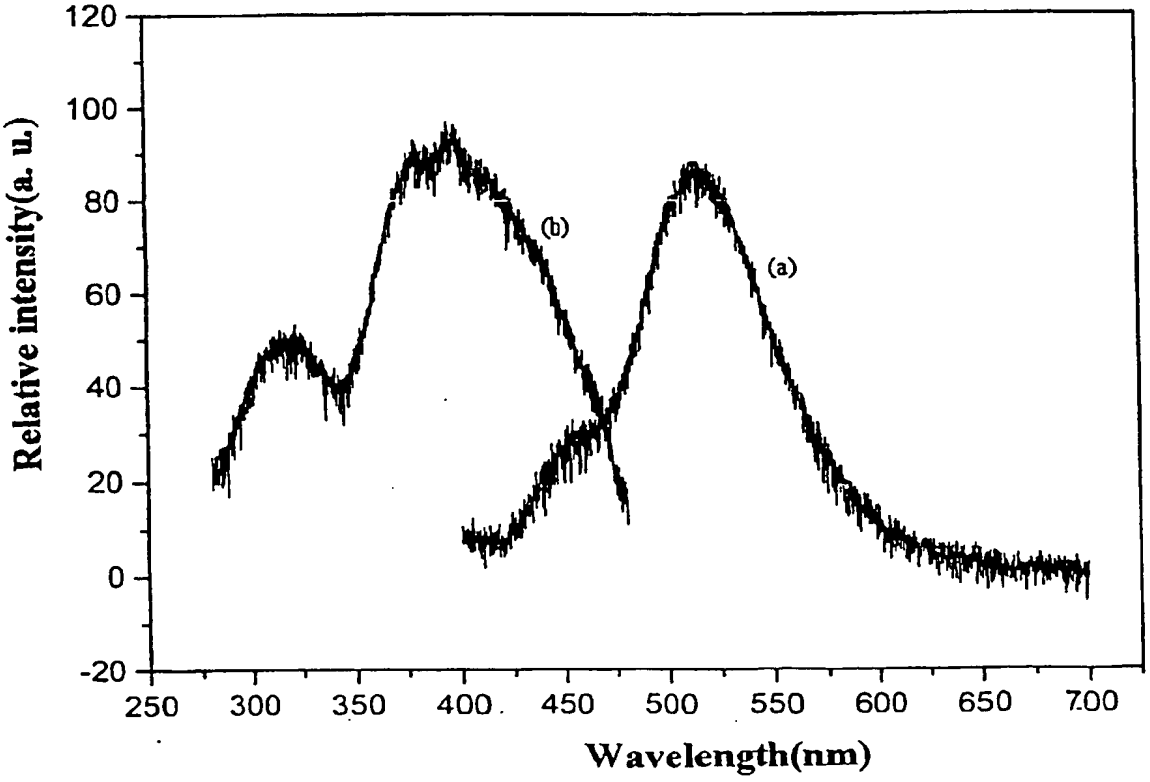


FIG.13

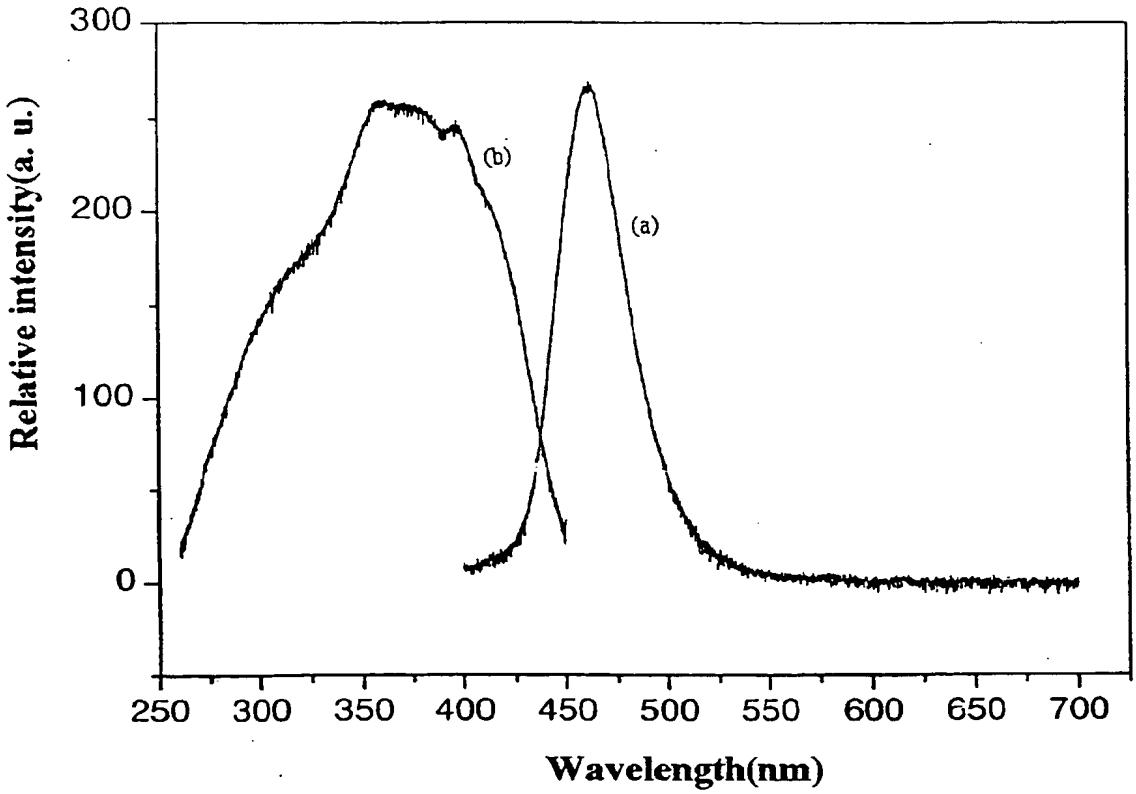


FIG.14

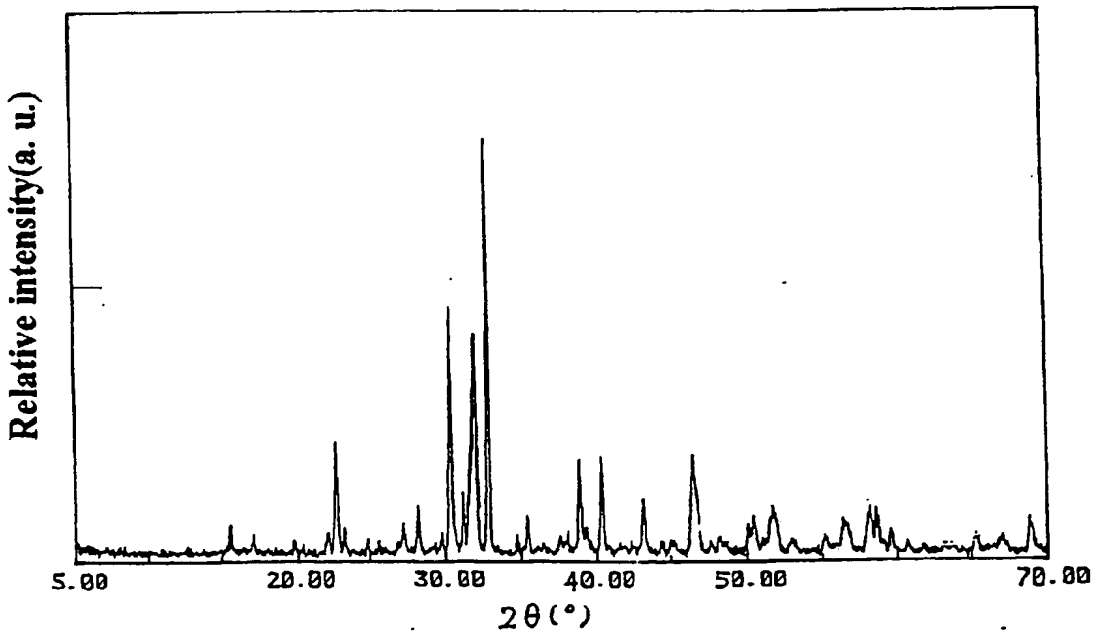


FIG.15

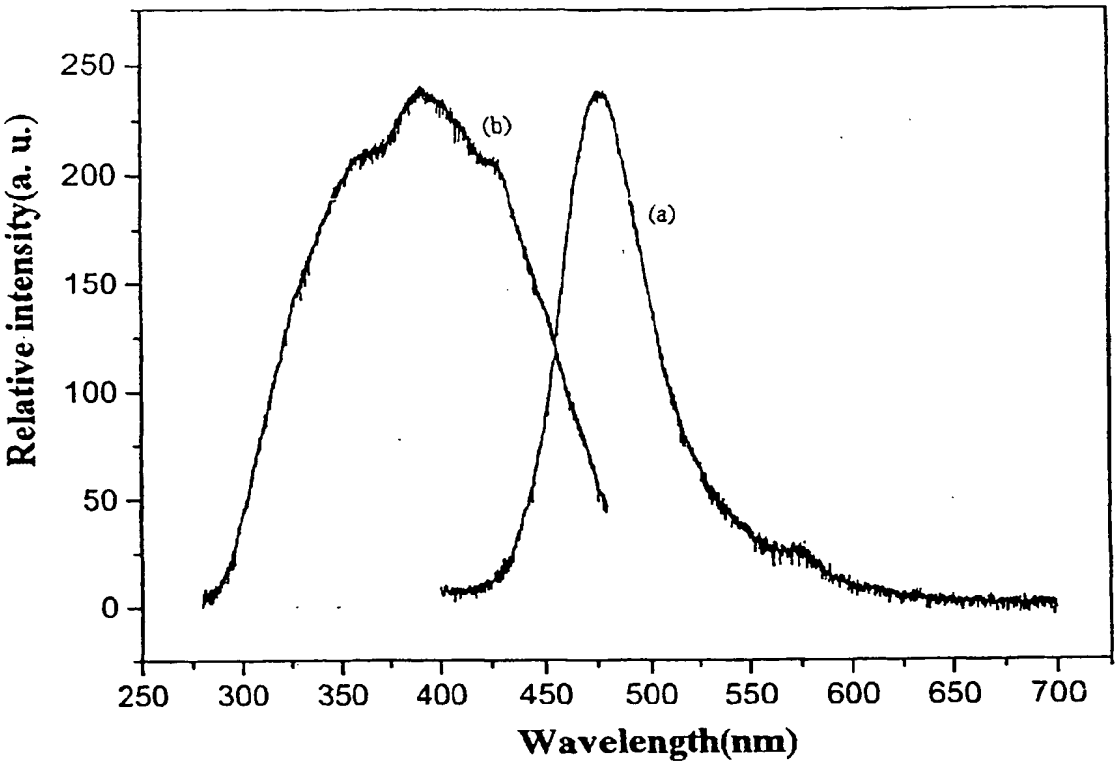

Relative intensity(a. u.)
250
200
150
100
50
0
(b)
(a)
250
300
350
400
450
500
550
600
650
700
Wavelength(nm)

FIG.16

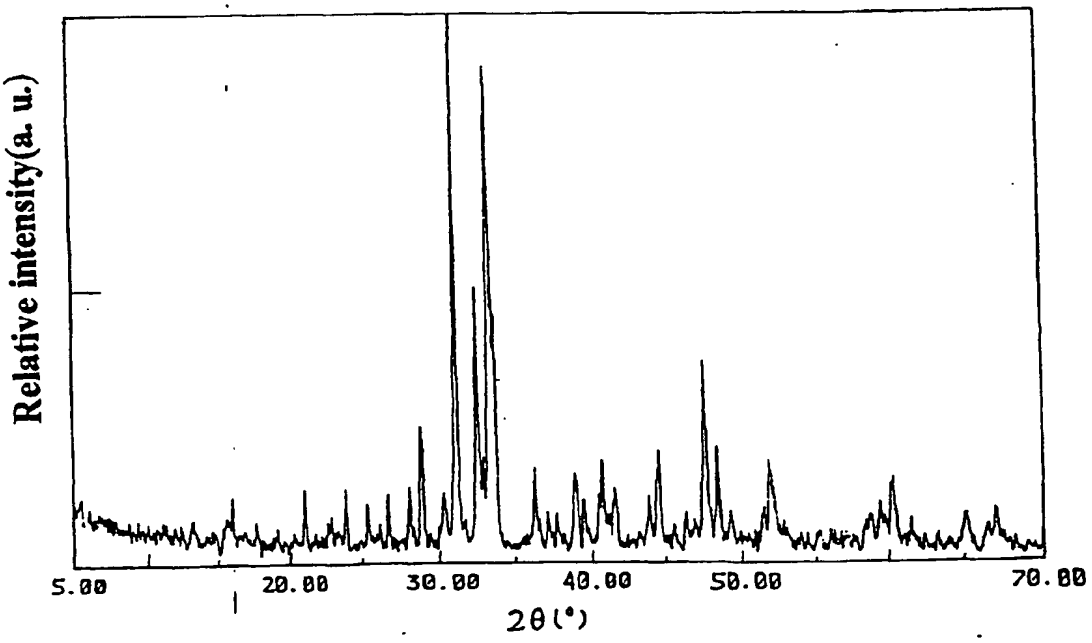
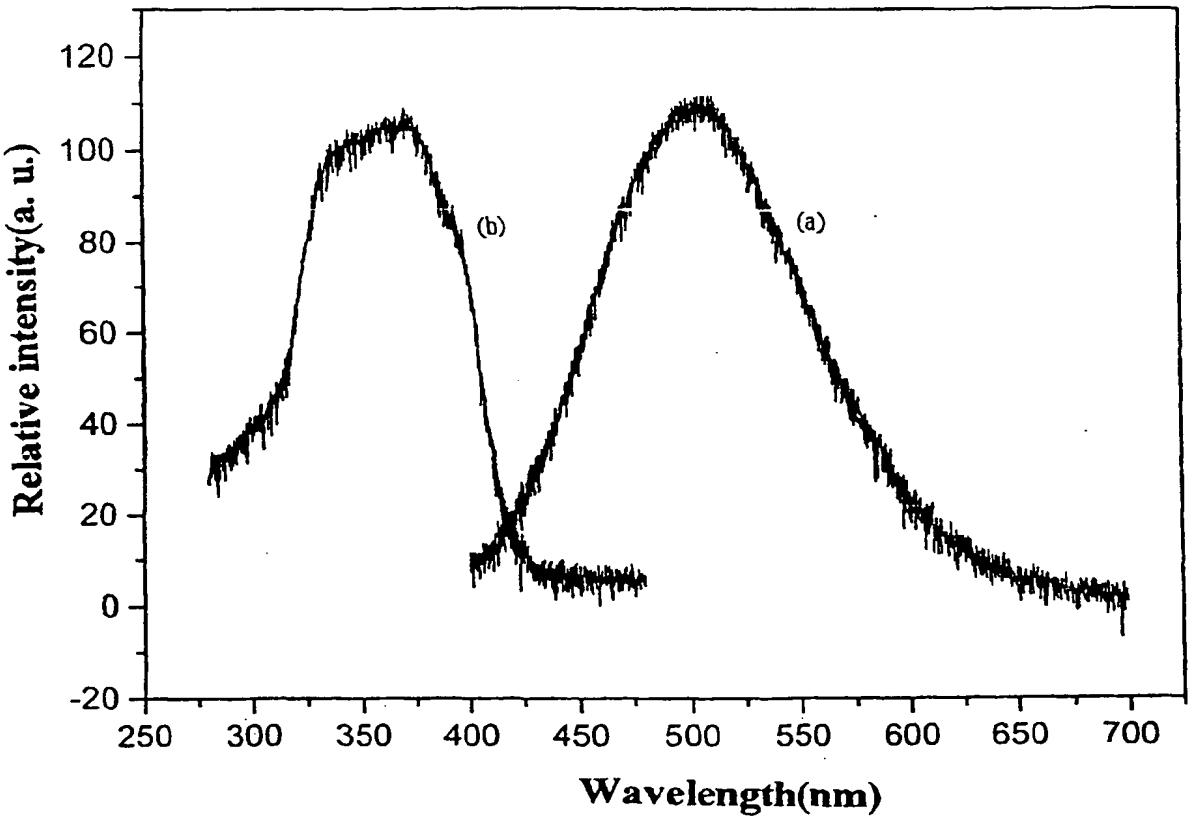

Relative intensity(a. u.)
5.00
20.00
30.00
40.00
50.00
70.00
2θ(°)

FIG.17


Relative intensity(a. u.)
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100
80
60
40
20
0
-20
250
300
350
400
450
500
550
600
650
700
Wavelength(nm)
(b)
(a)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN 97/00143

A. CLASSIFICATION OF SUBJECT MATTER

C09K 011/79

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched(classification system followed by classification symbols)

C09K 11/-

Documentation searched other than minimum documentation to the extent that such documents are included in the field searched

Electronic data base consulted during the international search(name of data base and, where practicable, search terms used)

REG, CAPLUS, WPI, CNPAT

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant claim No.
X	Philips Res. Rep. (1968), 23(2), 189-200 (Blasse, G.; Wanmaker, W. L.; Ter Vrugt, J. W.; Bril, A.)1 Feb., 1968 (01.02.68)	1-6,9-11
X	J. Alloys Compd. (1996), 241(1-2), 75-81 (Poort, S. H. M.; Reijnhoudt, H. M.; van der Kuip, H. O. T.; Blasse, G.)1 Jan., 1996(01.01.96)	1-6,9-11
X	Okayama Rika Daigaku Kiyo, A (1996), 32A, 65-71(guchi, Kazuhiro; Kakitani, Satoru; Miyake, Hiroshi) 01 Dec., 1996(01.12.96)	1-6,9-11
X	JP61-174291(Sony Corp.)5 Aug.,1986(05.08.86)	1-6,9-11
X	JP52-008994(Hitachi, Ltd.)24 Jan., 1977(24.01.77)	1-6,9-11
X	Gaodeng Xuexiao Huaxue Xuebao (Yao, Guang-Qing; Zhang, Liang; Su, Mian-Zeng)1 Jan., 1997(01.01.97)	1,9-11
A	WO93/25630A1(Thomson-CSF)23 Dec., 1993(23.12.93)	8
A	JP58-151322(Kasei Optonix, Ltd.)8 Sep., 1983(08.09.83)	8

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason(as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
16 Feb., 1998(16.02.98)	19.02.98
Name and mailing address of the ISA/ The Chinese Patent Office 6, Xitucheng Road, Haidian District, Beijing, 100088, China Facsimile No. 86-010-62019451	Authorized officer Huang, Qing Telephone No. 86-010-62093933

Form PCT/ISA/210(second sheet)(July 1992)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN 97/00143

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